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UNIVERSITY OF ALBERTA

THE FATE OF ADDED PHOSPHORUS IN CHERNOZEMIC AND LUVISOLIC SOILS.

BY

THOMAS MESSIER

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

SOIL FERTILITY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

FALL 1990

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DEDICATION

To my mom and dad, Mary-Rose and Raymond Messier, in appreciation of the constant love and support that you have given me.

To my dear wife Helen for your love and commitment.

Abstract

Low efficiency of P fertilizer can lead to excess input costs for the producer and to depletion of the Earth's supply of P ore deposits. This study was conducted to determine the fate of P fertilizer within the fertilizer zone in the season of application. A greenhouse experiment was conducted on samples from the Ap horizons of Breton (Othic Gray Luvisol) and Paddockwood (Dark Gray Chernozem) soils to determine the efficiency of ^{32}P uptake by barley and the distance of P movement from the fertilizer pellet site. The uptake of ^{32}P by barley was not affected by the granule size of monoammonium phosphate (MAP) fertilizer; however, when the granule of MAP fertilizer was placed inside a volume of peat or straw the uptake efficiency of ^{32}P by barley increased. Also, the efficiency of P uptake was greatly affected by the position of the band of MAP fertilizer. Deep bands 10 cm deep had significantly lower uptake of ^{32}P than bands located 2cm beside and 2cm below the seed row. The soil around the 0.10g granule of MAP fertilizer showed an increase in P to a distance of 1.5cm.

A follow up experiment focused on the zone of soil that interacts with MAP fertilizer. Five mg P/g soil was added to the two soils and equilibrated for 2 months; the soil solution was analysed and the solid P fraction underwent sequential extraction. Phosphorus mineral solubility diagrams indicate that brushite (DCPD), octacalcium phosphate and tricalcium phosphate were the minerals controlling $H_2PO_4^-$ activity in soil solution. The sequential extraction showed that P added as MAP fertilizer moved from readily available to less available soil P fractions with time. However, most of the added P remains in the readily available Resin-P fraction.

In the soil environment affected by MAP fertilizer added to Breton and Paddockwood samples, the Ca phoshate minerals control the $H_2PO_4^-$ activity and the added P remains readily available.

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1.0 Introduction

Phosphorus (P) is an essential element required for plant growth. It is classified, along with nitrogen, potassium, calcium, magnesium and sulfur, as a macronutient. Macronutrients are required for plant growth. Therefore, without an adequate supply of phosphorus, plant growth and crop production will be limited.

Phosphorus is most readily absorbed from soil solution as orthophosphate. The form of orthophosphate in solution is pH dependant (Figure 1.1). The highest rate of orthophosphate absorption into the plant occurs at pH 5 to 7 and therefore $H_2PO_4^{-2}$ is the most available form of P for the plant.

In addition to inorganic orthophosphate ions, plants may also absorb certain soluble organic phosphates. Nucleic acids were found to be as effective as monopotassium phosphate as a P source for barley growth on phosphorus deficient soils. However, the instability of the soluble organic phosphates in soil limits their importance as sources of phosphorus for higher plants under field conditions.

The concentration of P in plants varies from 0.1 to 0.4%. So a crop of 1000 kg/ha would contain 1 to 4 kg P/ha. This value is considerably lower than the concentrations of carbon, hydrogen, oxygen, nitrogen and potassium in plants. Dispite its low concentration in plants, P has a vital role in plant growth.

The most important role of P in plant growth is energy storage and transfer. Phosphate compounds store energy that has been derived from photosynthesis and the metabolism of carbonates. This energy is stored in adenosine di- and triphosphates (ADP and ATP), as high energy bonds between phosphate molecules. Almost every metabolic reaction in plants proceeds with energy derived from these phosphate derivatives.

In addition to this metabolic role, phosphorus is an important structural component of a wide variety of biochemicals. These biochemicals include nucleic acids, coenzymes, nucleotides, phosphoproteins, phospholipids, and sugar phosphates. The reproductive primordia of a plant requires adequate phosphate early on in development. P is essential for

FIGURE 1.1 - Removed because of copyright restriction.

SOLUTION pH

Figure 1.1. The effect of solution pH on ionic forms of dissolved phosphorus (Barber, 1984).

seed formation as it is found in large quantities in seeds and fruit. P is also involved in the structural framework of the protoplasm and thus occurs as part of the chloroplast structure.

Since P is important for the growth of plants, if plants are unable to attain adequate P from the soil, plant growth will be restricted. Without adequate P a plant may suffer from insufficient root growth and seed development. Resistance to diseases such as root rot will decrease. The plant will also be prone to lodging due to low straw strength.

The A horizons of Western Canadian soils contain significant amount of P (500 to 900 ug P/g soil). Dispite this high level of total P in many soils, available P tends to be low. This may be because P reacts with soil components to form relatively insoluble compounds, many of which have limited availability to plants. The major factor affecting the supply of phosphate to plants is the relationship between the amount of soil P (quantity) and the concentration of soil solution P (intensity). The quantity of total soil P (Pt) is much greater, in most soils, than the more important available P.

Fifty to one hundred years of cultivation under wheat-fallow systems have decreased the organic matter content of Western Canadian soils substantially. Mineralization of P during cultivation has increased its rate of removal from soil by crops. However, as the amount of organic matter decreases, the contribution that mineralization has for increasing the available P pool decreases. Therefore, with cultivation, increasing amounts of fertilizer additions are required to maintain crop production.

The addition of phosphate fertilizers to soils increase the plant available P content of the soil. Soils that are low in plant available P respond the best to fertilizer P additions. Upon addition to the soil, phosphate fertilizer is quickly integrated into the soil P cycle. Therefore, soils that have consistently received P fertilizers have experienced a buildup of soil P; with a relative increase in plant available P.

Understanding soil P and its response to fertilizer addition requires an understanding of the soil P cycle. P is present in this cycle as inorganic (Pi) and organic (Po) forms. The surface horizons of Western Canadian soils contain 25 to 55% Po. This Po is found in

humus and other organic materials. The Pi content of these soils is frequently higher than that of Po. Pi occurs in combinations with elements and clay minerals. Pi forms sparingly soluble to very insoluble complexes with iron, aluminum, and calcium. And the clay phosphate complexes are generally insoluble. The major processes of the P cycle are adsorption onto inorganic minerals, uptake by plants and microbial turnover through immobilization and mineralization. This transformation of soil P forms occurs under the balance of steady state conditions.

In this thesis the natural processes of the P cycle were studied to develop an understanding of the fate of fertilizer P once added to the soil. By studying both soil solution and solid phase characteristics resulting from the reactions of soils with P fertilizers, the nature of the fate of added P could be determined.

2. LITERATURE REVIEW

2.1 Phosphorus cycle in the soil

2.1.1. Introduction

Phosphorus (P) occurs in soil in many different forms. These different forms of soil P are components of the soil P cycle; depictions of the soil P cycle such as Figure 2.1 simply model the transformations of soil P between these different forms. In order to better understand the soil P cycle, the forms of soil P will be discussed along with possible transformation mechanisms.

2.1.2. Solid phase P

2.1.2.1. Organic P

The surface horizons of native Albertan soils contain 80-130 μg Po g^{-1} soil, while cultivated Albertan soils contain 70-80 μg Po g^{-1} soil (McKenzie, 1989). Only 50 - 70% of the Po forms have been identified (McGill and Cole, 1981; Stewart and McKercher, 1982). Factors complicating Po

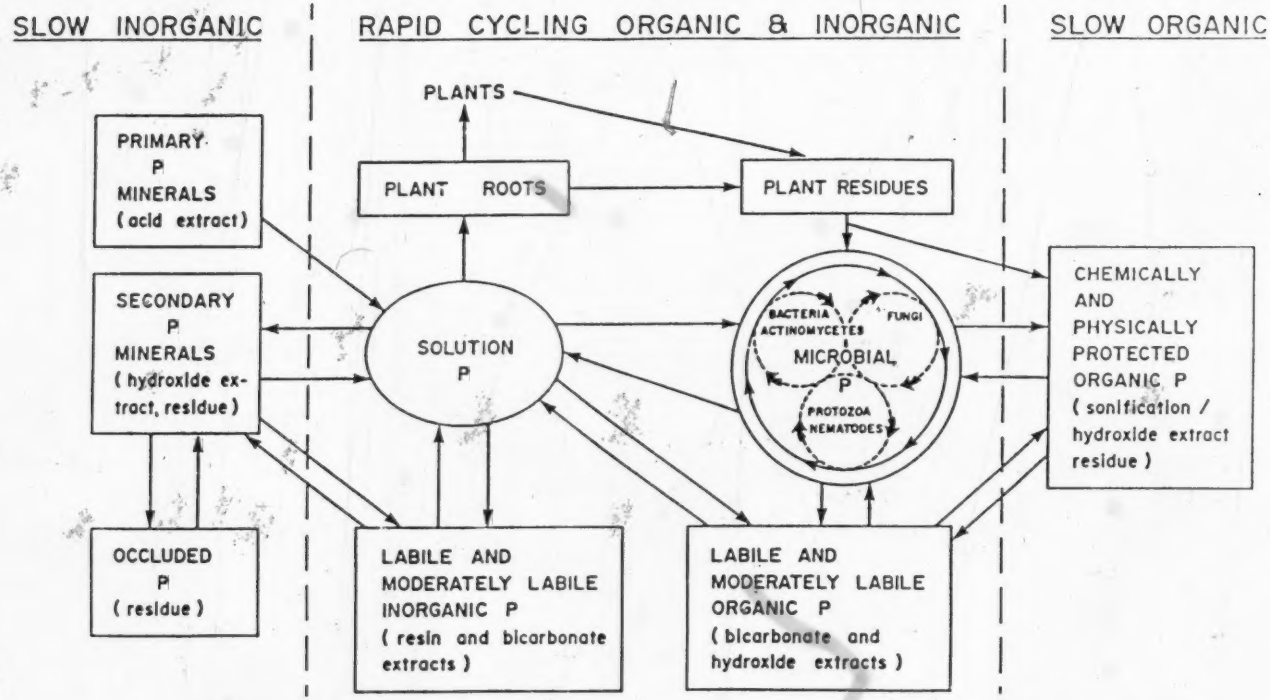
SLOW INORGANIC
RAPID CYCLING ORGANIC & INORGANIC
SLOW ORGANIC
PLANTS
PRIMARY P MINERALS (acid extract)
PLANT ROOTS
PLANT RESIDUES
SECONDARY P MINERALS (hydroxide extract, residue)
SOLUTION P
BACTERIA
ACTINOMYCETES
FUNGI
MICROBIAL P
PROTOZOA
NEMATODES
CHEMICALLY AND PHYSICALLY PROTECTED ORGANIC P (sonification / hydroxide extract residue)
OCCLUDED P (residue)
LABILE AND MODERATELY LABILE INORGANIC P (resin and bicarbonate extracts)
LABILE AND MODERATELY LABILE ORGANIC P (bicarbonate and hydroxide extracts)

Figure 2.1. The soil P cycle: Its components and measurable fractions. Source: Adapted from Chauhan et al.,(1981); extracts from Hedley et al.(1982).

identification include high chemical complexity of soil Po, strong suseptibility of some Po compounds to hydrolysis during extraction, strong sorption of Po by clays and insoluble salt formation with metal cations such as Al and Fe. Most Po has been identified as phosphate esters (Anderson, 1980) with a significant portion of polyphosphate compounds containing P-C, P-N and P-S linkages (McGill and Cole, 1981). The remaining Po probably occurs as insoluble complexes with clay and organic matter (Tate, 1985). Microbial P (Pm) represents a small but important labile pool of soil P (Jenkinson and Ladd, 1981) that is responsible for the redistribution of P through mineralization and immobilization.

Inositol phosphates (IP), nucleic acids and phospholipids are the ester forms that make up most of the Po in soil (Black, 1968). Since the plant does not affect phosphate, this ion enters into organic combination largely unaltered. Thus the P in IP, phospholipids and nucleic acids is found as phosphate (Alexander, 1977). IP comprising up to 60% of total Po are homocyclic compounds which can form a series of phosphate esters ranging from monophosphates to hexaphosphates. Penta-(IP5) and hexaphosphates (IP6) such as phytic acid are the predominant ester forms of this group found in soils (Halstead and McKercher, 1975). These higher inositol phosphates (IP5 and IP6) are more prevalent than the lower ester forms in more weathered soils (Halstead and Anderson, 1970).

Inositol phosphates are released slowly upon decomposition and are then quickly stabilized allowing them to accumulate to 25% of Pt. They are stabilized by reacting with Fe and Al under acid conditions and with Ca under alkaline conditions to form very insoluble salts. Soil IP contents are found to be significantly correlated ($r = 0.91$) with acid oxalate-soluble iron but not with organic carbon (Alexander et al, 1974). These complexes are more resistant to enzyme attack than more soluble ester salts. Clay minerals and finely divided sesquioxides will strongly adsorb hexaphosphate (Alexander et al, 1974). Phytase enzymes cause IP breakdown through dephosphorylation by attacking a phosphate group adjacent to

the free hydroxyl provided that it is not sterically attached as an axial group (Irving and Cosgrove, 1971). The activity of phytase is reduced by IP retention by Fe and Al complexes in acid conditions and retention by clays in neutral conditions (Alexander, 1977).

RNA and DNA occur in all living organisms and consist of a chain of sugar units, joined by phosphate ester bridges. A nitrogen base is then attached to each sugar molecule. The evidence for the existence of nucleic acids in soil is indirect. The presence of nucleic acid bases in a bound form in humic acid fractions, and the proportion in which they occur are indicative of DNA derived polynucleotides of microbial origin (Halstead and McKercher, 1975). Upon residue decomposition these nucleic acids are quickly released into soil, accounting for 5 - 10% of Po, and subsequently broken down. Mineralization proceeds by an initial depolymerization of nucleic acids and then subsequent cleavage of the phosphate from the products generated by the depolymerizing enzymes (Alexander, 1977).

Phospholipids are esters of fatty acids containing P and comprise 1% of Po. The concentrations of lipid P were highly correlated with Pt and soil organic carbon in a study in Saskatchewan (Halstead and McKercher, 1975). It has been shown that actinomycetes are the major organisms responsible for decomposition of phospholipids in soil organic matter. Phosphate is cleaved from the organic compound, and it is then assimilated by responsible populations (Alexander, 1977). However, phospholipids may also be adsorbed to soil constituents (McGill and Cole, 1981). The importance of this group of P compounds in supplying P to plants cannot be overlooked since their synthesis and degradation may be fairly rapid in the soil system.

Other esters that originate from the breakdown of bacterial cell walls tend to be stable in soils. In addition, other as yet unidentified components may be formed by microbial action (Alexander, 1977).

Studies of Po mineralization in soil are not numerous because of the uncertainty of identifying the origin of Pi, since both Po and Pi forms occur simultaneously. Easily soluble Po can be converted to Pi relatively quickly by phosphatase enzymes (Cole et al, 1977).

These enzymes are released into the soil by microbes and plant roots (Tarafdar and Jungk, 1987; Tarafdar and Classen, 1988). The observation that Po is more variable in soil organic matter than are N and S (Dalal, 1977) suggests that Po may be stabilized by mechanisms other than those stabilizing organic matter in general. The biological activity that regulates the simultaneous mineralization and immobilization of P is affected by available C, available nutrients, temperature, water content and soil chemical factors such as pH.

Carbon from growing roots and dead plants is a major source of energy for microbes. The balance between mineralization and immobilization of P during organic matter breakdown depends on the C:P ratio of the substrate being utilized by the microorganisms (White, 1981). Chauhan et al (1979,1981) determined that the rate of residue decomposition affects the rate of P immobilization according to the energy released and the C:P ratio of the residue.

The amount and type of carbon source in the soil affects the rate of P immobilization. Cellulose produces a lower amount of energy when decomposing and therefore will decompose at a slower rate than simple sugars. However, cellulose decomposition has a higher capacity to immobilize P (Singh et al, 1988); because fungal flora, which are the more active organisms in cellulose degradation (Alexander, 1977), assimilate 15 - 20% more carbon than bacteria and actinomycetes and therefore use more N and P. Nevertheless, slower decomposition of cellulose means a slower rate of P immobilization thus leaving larger amounts of available P during initial growth when plants need very high amounts for their proper growth (Singh et al, 1988). Readily oxidizable carbonaceous compounds proved harmful to the growing plants because they rapidly immobilize very high amounts of available P during initial stages of growth. Cellulose and crude fiber, both easily available to farmers in the form of crop wastes, initiate a slow rate of P immobilization but the process continues for a long period of time.

When fertilizer P is added with cellulose, 58 - 69% of the added P was found in Pi forms (Chauhan et al, 1981). The addition of P fertilizer without a carbon substrate

followed by incubation does not significantly alter the Po content of soil and the added P remains in inorganic forms. Readily plant available P was greatly increased by addition of fertilizer P. But when carbon was added with the fertilizer P, the increase in labile P indices were as great as when P fertilizer was added alone (Chauhan et al, 1981).

Mechanisms involved in the interaction of the major nutrients are very complex, making predictions of P transformations based on such interactions difficult (McGill and Cole, 1981). The Po level is known to be directly related to the concentration of other humus constituents. The P content of humus is 0.3 to 1.0% and 5 to 20% of the C and N concentration, respectively (Alexander, 1977). However, Spiers and McGill (1979) detected an increase in phosphatase activity with the addition of N, S and C but not with the addition of P.

The plant availability of P in crop residue is governed by warmer temperatures and adequate available moisture levels (Abbott, 1978). Seasonal fluctuations of Po have been observed in cultivated soils (Dormaar, 1972), where soil Po increases over winter and decreases in spring. Campbell et al (1984) observed several significant flucuations of Pi during the growing season, which are correlated to air temperature and soil moisture.

Soil organisms function over a wide range of water contents (Wilson and Griffin, 1975), therefore decomposition of organic residues occurs over a similarly wide range of water contents. Campbell (1973, 1976) found peaks in microbial activity after rainfall, indicating that wetting and drying affects both mineralization and immobilization.

Po is less stable in neutral or alkaline soils than in acid soils because microbial diversity decreases with decreasing pH (Tate, 1985). Mineralization of Po increased with rises in soil pH but mineralization of organic carbon and total N does not. These same pH effects on mineralization in the field are indicated by the fact that ratios of total organic carbon and total N to total Po increase with pH in the same soil samples.

P occurs in soils in a number of inorganic and organic forms. The complex

transformations of these forms are affected by a combination of physical, chemical and biological reactions. C and N levels help the microbial population to redistribute P through mineralization and immobilization.

The P of this organic pool in virgin soils is derived from primary P minerals. For a better understanding of the P cycle the forms and solubilities of these minerals should be examined.

2.1.2.2. Phosphate minerals

P is pentavalent in nearly all naturally occurring phosphates. The crystal structures of P minerals have the P atom surrounded by four atoms forming an approximate tetrahedral arrangement. The formation of stable atomic structures containing PO_4 tetrahedra is accomplished through the high affinity of PO_4 for cations exhibiting 8-fold coordination. This results in mineral species that can be classified by a system similar to that used for silicate minerals - ie) framework, chain, layer phosphates. The most common naturally occurring phosphate minerals are the Berlinite, Variscite, Apatite and Crandallite groups.

The Berlinite group is homostructural with quartz. This framework group has PO_4 and AlO_4 tetrahedra linking and alternating along verticies.

The Variscite group has a framework structure and is widely distributed in nature. Variscite and strengite are end members of this isomorphous series, the composition of which varies from $Al[PO_4](H_2O)_2$ to $Fe[PO_4](H_2O)_2$, respectively (Lindsay and Vlek, 1977).

The Apatite group has an insular structure consisting of columns of Ca and O atoms parallel to the unique axis forming trigonal prisms. A detailed description of the structure of apatite is given by Kay et al (1964). From structural and compositional studies of natural materials it has been found that many substitutions are possible in the general formula ($Ca_2Ca_3[PO_4]_3(OH,F)$) of apatite. Only OH and F show perfect isomorphism in the anionic substitution of Ca(II) trigonal prisms resulting in the end members of the isomorphous series. An extensive listing of apatite subgroups is given by Kreidler (1967).

Florapatite is the accessory mineral of igneous rocks and is the primary enriched

phase of carbonatites. Francolite is the primary marine phosphate in sedimentary rock. Dalhite makes up the mineral matter of fossil bone; and hydroxyapatite is found in guano-altered limestone (Lindsay and Vlek, 1977).

The Crandellite group has insular structure with P occupying a tetrahedra position and Fe or Al an octahedral position. The third position is filled from a group of a large number of cations. Gorceixite and crandellite are common forms of soil phosphate as they are present in the clay fraction of a variety of soils (Lindsay and Vlek, 1977).

The persistence of apatite in soils depends on the intensity of weathering by geochemical and biological processes. In neutral to alkaline environments of high Ca concentration, apatite is stable and weathering is probably limited to the somewhat acid environment adjacent to plant roots. In more humid regions, where acidity is a consequence of soil formation and development, apatites dissolve rapidly, releasing their phosphates into soil solution (Tiessen and Stewart, 1983). Most of the P enters Fe and Al minerals by substituting for silicate. However, Lajtha and Schlesinger (1988) found in their study of a chronosequence a decrease in Ca-P but did not find a corresponding increase in Al-P or Fe-P with increasing soil age. In soil, P ions can also react with solution Al or Fe to form stable secondary minerals. These minerals are comparatively stable under acid conditions. The low solubility of these minerals not only limits the leaching loss of P but also its availability to plants.

Insoluble inorganic phosphates are known to be solubilized by different genera of bacteria, fungi and actinomycetes (Hayman, 1975). Phosphate solubilizing microbes have been used extensively in Eastern Europe to increase availability of native soil P (Mishustin and Naumova, 1962). The important mechanisms involved in the dissolution of insoluble phosphates in soil include formation of organic acids and chelating substances. The increase in microbial activity as a result of composting produces these organic acids and chelating substances and has been shown to increase the solubilization of rock phosphate (Mishra and Bangan, 1986) The rate of P mineral dissolution is influenced by the

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concentration of calcium and P in the soil solution (MacKay et al, 1986).

The use of phosphate solubility diagrams has become well established for describing P mineral solubility in the soil environment (Aslyng, 1954; Lindsay et al, 1959; Lindsay and Moreno, 1960; Rai and Lindsay, 1975). Solubility diagrams are constructed by including ion activities in a minerals' equilib m reaction. The isolines are plotted as the relationship between pH_2PO_4 and pH.

Solubility isolines are particularly useful for determining relative stabilities of phosphate compounds in soils at various pH values. A supersaturated solution indicates precipitation and an undersaturated solution indicates dissolution. These solubility isolines have been quite useful in indicating the solid phase calcium phosphates that control soluble P levels.

However, the thermodynamically generated chemical transformations characterized by under- or supersaturated conditions take place very slowly. Soil scientists have tended to think of crystalline phases in soil as pure stoichiometric crystals, when in fact such purity is difficult to obtain in an environment as heterogeneous as soil. Isomorphous substitution is a wide occurrence in soil minerals whether of geologic or pedogenic origin. Solubility product isotherms represent end members in an isomorphic substitution series of minerals. For the purpose of assessing soil P, solubility product isolines can be excellent tools in determining the kind of P compound that influences P in the soil solution and possibly delineating the path by which P is supplied to a growing plant. However, solubility product isotherms cannot measure the quantity of such compounds, and this is a serious limitation.

Fertilizers can be supplied to the soil in mineral form; largely as monoammonium phosphate (MAP) and as monocalcium phosphate (MCP). As dissolution of water-soluble fertilizers proceeds in soils, conditions often favor in situ precipitation of P compounds. The best documented examples of such reaction products are the Brushite ($CaHPO_4 \cdot 2H_2O$) residues remaining at application sites of MCP fertilizers. Lehr et al (1959) placed MCP granules in five soils at two moisture contents and found that from 20 - 34% of the applied

P remained as brushite. With time these reaction products of brushite change to octacalcium phosphate (OCP) (Lehr and Brown, 1958; Bell and Black, 1970b). The soil property most widely used to predict the ultimate reaaction products is soil pH, recognizing that pH is itself a reflection of degree of weathering, minerals present, exchangeable cations, and a multitude of other factors.

The solubilities of P fertilizer reaction products have also been described by solubility diagrams. These crystalline minerals are generally much more soluble than the primary P minerals. The more soluble reaction products are more likely to be a source of P for plants than selectively adsorbed P. Since labile phosphate and crystalline phosphate coexist in equilibrium: Labile P → Solution P → Crystalline P.

2.1.2.3. Adsorbed P

P sorption occurs on the surfaces of soil constituents of either constant charge or variable charge. Iron and aluminum oxides, amorphous clay minerals and organic matter all have surfaces that allow H^+ and OH^- to determine the surface charge. Whereas, crystalline clay minerals have largely a permanent negative charge through isomorphous substitution. These secondary clay minerals interact through cations held tightly to platelike surfaces.

Hydroxyoxides of Fe and Al are amphoteric, having either negative, neutral or positive charge depending upon pH. As the pH in the soil decreases, the edge hydroxyl groups become HOH groups. By calculating the number of hydroxyls released through exchange, Rajan et al (1974) determined the adsorption of HPO_4 by hydrous Al oxides to be due to a binuclear coordination of phosphate ions with two Al atoms. Therefore it is well established that ligand exchange is the most likely mechanism of the phosphate - surface hydroxyl reaction (Parfitt et al, 1975; Goldberg and Sposito, 1985). The result of this exchange reaction is the formation of an inner-sphere surface complex (Sposito, 1981b) between an o-phosphate group and a metal cation which is bound to the hydroxyl group.

Barrow (1985) expanded earlier models of adsorption onto variable charged surfaces

with a four-layer model. The innermost layer contains adsorbed H^+ and OH^- ions. These are responsible for the charge development. The next layer contains adsorbed ions. The ions of this second layer differ not only in their affinity for the surface but in their mean position when adsorbed. The closer the anion adsorption plane is to the surface plane the greater the effect of decreasing anion adsorption with increasing pH. Thus, in this model the location of the adsorption plane determines the steepness of the effect of pH and also the magnitude of the charge conveyed to the surface. The third layer consists of electrolyte ions (eg: Na^+, Cl^-) bound to surface groups. The fourth layer is the diffuse layer.

Hematites may absorb widely different amounts of phosphate according, not only to their specific surface but to their shape; because shape is related to the relative extent of the different adsorbing and non-adsorbing faces (Barron et al, 1988). A theoretical mean adsorption value of phosphate on goethites is about 2.5 umol P m^{-2} (Goldberg and Sposito, 1984b), while hematites generally sorb two and a half times less phosphate (Schwertmann, 1987).

Pissarides et al (1968) determined that clays saturated with divalent ions adsorbed more P than clays saturated with monovalent ions. This indicates the thickness of the diffuse double layer may be involved in controlling how much P is adsorbed at the surface of the clay. Hingston et al (1972) postulated that the edge faces of kaolinite behave similarly to the hydrous oxides in anion adsorption. The adsorption of low phosphate concentration onto kaolinite is a result of the replacement of specifically adsorbed water molecules at the broken edge of the clay lattice. Kuo and Lotse (1972) believe that phosphate replaced a water molecule rather than a hydroxyl group, since the pH of the solution did not significantly rise during the reaction.

Adsorption of P by soils is influenced by the species and concentrations of cations in the system. Divalent cations enhance P sorption relative to monovalent cations. For example calcium saturated clays have more accessible positively charged edge sites. And 1 meq of exchangeable Al/100g soil when completely hydrolysed may fix up to 102 ppm of P

in solution. Also both inorganic and organic anions can compete with P for sorption sites. Organic anions which form stable complexes with Fe and Al of soil components are paticularly effective in reducing P sorption.

P adsorption has been found to correlate with the organic carbon content of soils. This correlation results from the exchange of P anions with hydroxl groups in organic matter and from the effect of P adsorption by Al and Fe associated with organic colloids. Since humus is normally negatively charged, it is not thought to retain much P by itself in soils. However,significant amounts of P are retained by organic matter that is associated with Ca, Fe and Al. For example, when manure was added over a long period of time, Weir and Soper (1963) detected an increase in Fe associated P. Also humic acid reacts with Al from soil minerals to form hydroxyl-Al-humic acid complexes which give rise to new surfaces for P adsorption (Appelt et al, 1975).

Calcium carbonate develops a negative charge due to the greater tendancy for Ca ions than CO3 ions to go into solution. Phosphate ions then become chemisorbed at the surface. This reaction of P with calcite surfaces involves absorption of small amounts of P followed by precipitation of calcium phosphate (Griffin and Jurinak, 1973, 1974). The initial adsorption is thought to occur at certain sites where phosphate ions form clusters which act as nuclei for subsequent crystal growth. Impure calcites and those of high specific surface result in more adsorption of P and more rapid formation of calcium phosphate precipitates. Therefore, phosphate activity will be lower in those soils that have a high calcium activity, a large amount of calcium carbonate and/or a large amount of calcium saturated clay.

2.1.3. Soil Solution P

2.1.3.1. P form in soil solution

Plant roots absorb P from soil solution. Therefore, an understanding of the forms of P in soil solution and mechanisms that maintain adequate concentrations are important.

P is a component in soil organic matter. When soluble organic complexes are present they will contribute to the total P in soil solution.

Polyphosphates form several ionic species in solution. The $H_2P_2O_7$ and the HP_2O_7 ions are the predominant polyphosphate species in solution in the pH range of most soils. Polyphosphates are metastable in soils and hydrolyse to orthophosphate.

Phosphate ions, ions pairs, and complexes are present in soil solution, but the orthophosphates are the most stable forms. The pH dependancy of orthophosphate species allows for the calculation of the activity of any one of the orhtophosphoric acid species when the P concentration in solution is known (Figure 1.1). Phosphate combines with many of the di- and trivalent cations to form ions pairs and complexes. Whenever ionic activities are calculated from total P in solution, these ion pairs and complexes must be considered. P is absorbed by plants largely as primary and secondary phosphate ions (H_2PO_4 and HPO_4), which are present in solution.

2.1.3.2. Phosphate concentration required by plants

Maintainence of adequate concentrations of orthophosphate ions in soil solution is essential to plant growth. Classen and Barber (1974) use kinetics to depict a plants dependance upon the P concentration in soil solution. The required phosphate concentration in soil solution depends primarily on the crop species and the level of production desired. Tisdale et al (1985) list a range of phosphate concentrations required for the growth of a variety of crops, ranging from 0.003 to 0.3 ppm, with wheat requiring 0.01 to 0.03 ppm. Also, the optimum phosphate concentration varies with the stage of growth and the occurrence of stress.

Maintainence of adequate phosphate concentration in soil solution depends on the solid phase P entering into solution to replace the amounts withdrawn by plant uptake. There are two different theories explaining the relationship between solid and solution phase P. The first describes the quantity (Q) of soil P as the amount of P in the solid phase that acts as a reserve and the intensity (I) refers to the phosphate concentration of soil solution. The second theory depicts an equilibrium reaction between soil solution P and two levels of solid P, the labile and non-labile fractions (Barrow, 1980). The labile soil P is the readily

available P that permits rapid dissociation. The depletion of labile P initiates the slow movement of non-labile P to labile P.

2.2. FATE OF FERTILIZER P WITHIN THE P CYCLE

2.2.1. Soil-Fertilizer P Reaction

2.2.1.1. Introduction

When P fertilizers are added to the soil nearly saturated solution of the phosphorus fertilizer material forms in and around fertilizer granules. Osmotic potential differences bring more water to the P saturated solution causing fertilizer solution to move to the surrounding soil (Khasawneth et al, 1974). As the saturated solution of phosphorus salts move into the first increments of soil, the chemical environment is dominated by the solution properties rather than by the soil properties. The soil components alter their solubilities as a result of the ion charge and pH changes caused by the fertilizer solution. This increased solubility of soil components will then allow for a flush of cations to enter the solution thus altering the solution composition.

2.2.1.2. Sources for Reacting Ions

The soil acts as a sink for the ions in the fertilizer solution and also as a source of reactive cations. The major source for basic cations is the exchange complex. The sum of exchangeable cations varies from 1cmol(+)/kg soil on coarse textured soils to 50 to 60 cmol(+)/kg soil on fine textured soils. The exchangeable ions in productive agricultural soils are almost always $Ca^{2+} > Mg^{2+} > K^{+} = Na^{+}$ (Bohn et al, 1987). Sposito et al (1983a,b) determined that montmorillonite clays did not express differences in exchange isotherms of basic cations. However, when organic matter is present, the exchange isotherms indicate a preference of the soil for calcium and magnesium over sodium, and for calcium over magnesium.

While the exchange complex is the source for the basic cations, metal ions like silicon, iron, aluminum and manganese are derived from the soil mineral constituents. The low pH of saturated MAP fertilizer solution will initiate the dissolution of Al, Fe and Mn oxides releasing these cations into solution. Also some sol minerals near the fertilizer site may undergo dissolution, placing relatively large quantities of reactive cations (Al, Fe and Ca) into solution (Lehr, 1972). Lindsay and Stevenson (1959a,b) found large concentrations of Al and Fe in the fertilizer solution. As all these ions enter solution, their reaction with the added phosphate would seem iminant.

2.2.1.3. Thermodynamics of Phosphate Reactions

With the dissolution of phosphate fertilizer granules, ion activities in soil solution become supersaturated with respect to many phosphate minerals. The soil matrix acts as a source of water for granule dissolution and as a sink for the fertilizer solution (Bouldin et al, 1960). As sucessive increments of soil are contacted by the moving front of fertilizer solution, soil derived cation concentrations build up both from the replacement of exchangeable cations and from the dissolution of soil minerals (Kittrick and Jackson, 1955 & 1956). These ions in solution can react with fertilizer phosphate to precipitate as phosphate minerals.

When the ion activity product of a mineral is greater than its solubility product, the solution is supersaturated with respect to that mineral. When a solution is supersaturated thermodynamics indicate that the mineral in question precipitates; likewise when a solution is undersaturated thermodynamics indicate that the mineral in question should be undergoes dissolution. Therefore, when a mineral is in thermodynamic equilibrium with a solution, the ion activities in solution will correspond to the solubility product of the mineral in question.

Phosphate mineral solubility isolines are a way of depicting how mineral supersaturation values change. The construction of these curves requires the calculation of the free ionic concentration in solution by taking into account ion-pair and complex

formation. To calculate these ion activities in the presence of multicharged ions, an extended form of the Debye-Huckel (Davies, 1962) may be used.

Solutions containing calcium and phosphate are very complex as many mineral phases become supersaturated. The possible solid phases resulting from these solutions, in order of increasing solubility, are: Hydroxyapatite (HAP), $Ca_5(PO_4)_3OH$; whitlockite (W), $Ca_4H(PO_4)_2$; octacalcium phosphate (OCP), $Ca_4H(PO_4)_3 \cdot 2.5H_2O$; monetite (M), $CaHPO_4$; and Brushite (B), $CaHPO_4 \cdot 2H_2O$. In addition to these crystalline forms there is an amorphous phase (ACP) of probable composition $Ca_3(PO_4)_2 \cdot xH_2O$. Since kinetics is a determining property in addition to thermodynamics, often the solid phase that precipitates first undergoes changes in solution towards phases of higher stability.

2.2.1.4. Nucleation of reaction products

The precipitation process, therefore, involves more than thermodynamics, as can be determined by figure 2. The first stage, nucleation, corresponds to the production of new centers from which mineral growth can occur. Phosphate minerals then form either through crystal growth or by the aggregation and coagulation of crystallites. Therefore, without nucleation phosphate mineral precipitates cannot occur. It is thought that every mineral has a critical limit of supersaturation (Nancollas, 1984) or formation product (Abbona et al, 1986) that allows for the initiation of the process.

Knowledge of nucleation rate in addition to supersaturation, seem to be required to understand the dynamics of phosphate mineral formation. Minerals such as Brushite with higher solubilities but lower critical supersaturation values than minerals like HAP, often form in solutions that are metastable with respect to HAP. Therefore, these metastable solutions support a higher $H_2PO_4^-$ activity than what would be expected by thermodynamics (ie. the most stable minerals controlling solution P activity).

Abbona et al (1988) found that in calcium and magesium phosphate solutions, Brushite and monetite occur as the final precipitate phases,even though only monetite is thermodynamically stable. Brushite owes its wider occurrence to its higher nucleation rate,

and its persistence in solution to the high value of the critical supersaturation of monetite. The precipitation of the ACP is usually accompanied by the nucleation of Brushite. While the Brushite crystals precipitate, the amorphous phase dissolves at a rate which is related to the growth of Brushite crystals.

Therefore, the calcium phosphates which precipitate first in solutions of high to medium concentration do not always have the highest supersaturation values (Abbona, 1988). For example, soluble minerals like brushite and ACP usually form before stable minerals like HAP because their lower formation product values offset the high supersaturation values of HAP. Abbona et al (1988) also found that no major changes occured in these metastable solutions with respect to brushite.

2.2.1.5. Nature of reaction products:

Brushite ($CaHPO_4 \cdot 2H_2O$) is the most important product of precipitation in moderately acid solutions of $4.0 < pH < 6.0$. Lundager Madsen (1984) found that supersaturated solutions produced precipitates of (1)brushite, (2)monetite, (3)OCP, (4)amorphous TCP. Brushite was found to be a precursor of OCP, serving as a substrate for the latter. At $pH > 6$, brushite is unstable with respect to OCP; the transformation takes place in a few hours, but is usually preceded by an induction period which may amount to several days (Lundager Madsen, 1984). The final products seem to be metastable with respect to more stable phases.

One of the peculiarites of the aqueous calcium phosphate system is the occurrence of an amorphous phase. It is generally recognized that it is formed in the higher pH range and that it is a hydrous tricalcium phosphate ($Ca_3(PO_4)_2 \cdot xH_2O$). ACP is also thought of as the critical nuclei of whitlockite. ACP has also been reported to contain Mg when precipitated from solutions containing Mg. ACP is metastable over the whole pH range and may be formed simultaneously with crystalline precipitates.

Knowledge of the conditions for precipitation of ACP is essential for understanding the behavior of supersaturated calcium phosphate solutions, since it strongly influences the

occurrence of domains of other phases (Lundager et al, 1986). For example, as ACP precipitates Ca and P are consumed and pH decreases; this reduces the supersaturation of other calcium phosphates often below the critical value of supersaturation. However, brushite, struvite and calcium oxalate were often observed to crystallize more or less simultaneously with the formation of ACP (Lundager et al, 1986).

When Mg is in high concentration in phosphate solutions struvite ($MgNH_4PO_4 \cdot 6H_2O$)and newberyite ($MgHPO_4 \cdot 3H_2O$) are often the main reaction products (Abbona et al,1982). However, dispite the fact that solutions of Mg, NH4 and H2PO4 easily form supersaturated systems, newberyite and struvite in general do not precipitate under low supersaturation values (Abbona et al, 1982). Struvite precipitates alone or with the other phosphates depending upon the pH and solution composition. Struvite solubility and nucleation are affected by the phosphatic species which is dominant at the pH of the solution. Therefore the nucleation of minerals in such solutions is mainly controlled by thermodynamic parameters (Abbona and Boistelle, 1985).

Traces of Mg added to calcium phosphate solutions supersaturated with respect to HAP, TCP, OCP, and brushite reduce the rate of calcium phosphate crystallization and delay the transformation of ACP to more stable phases. The Mg ions kinetically hinder the nucleation and subsequent growth of calcium phosphate minerals by competing for lattice sites with the chemically similar but larger Ca ions. Salimi et al (1985) noted that although the presence of Mg ions markedly retards the rate of seeded OCP crystallization, there was no detectable effect on the rate of brushite formation. Where Mg ion concentrations are appreciable the marked reduction in the rate of OCP crystallization may stabilize the more acidic hydrated calcium phosphates such as brushite during precipitation reactions. Therefore, the numerous observations that brushite is a viable phase may be traced to the Mg^{2+} ion concentration in these systems.

The precipitation products found in pure calcium phosphate solutions are also found when phosphate solutions are added to soil or soil solutions. Moreno, Brown and Osborne

(1960) found that, at 25 C, brushite hydrolysed to OCP in soil solutions with a pH value of 6.38 or higher and that this hydrolysis reaction increased with increasing pH. They found that OCP was metastable with respect to HAP. Bell and Black (1970a) detected OCP 4 weeks after brushite was added to the soil, however they could not detect the more stable HAP in the soil even after 44 weeks. This hydyloysis of brushite to OCP was noted to be inhibited by the presence of a soil solution concentration of Mg of 10^{-3}M. In the presence of soil solution Mg, struvite and newberyite precipitate in addition to brushite (Bell and Black, 1970b; Racz and Soper, 1967; Lindsay et al, 1962).

2.2.1.6. Mobility of Added Phosphate

Khasawneh et al (1974) found that when P fertilizers were banded at a rate of 112kg P/ha, P moved up to 3cm from the pellet with most of that P approximately within 1.5 to 2cm from the band. When Bell and Black (1970b) placed 2.28 g MAP on top of a column of soil, the P fertilizer was detected 2.6cm down in a SiCL soil. They noted that P movement was lower in soils with montmorillonite than in soils with kaolinite or vermiculite as the dominant clay mineral.

However very few researchers have been able to establish the presence of precipitated reaction products at varying distances away from a fertilizer using direct methods. Bell and Black (1970a) identified traces of Brushite and Struvite 3 to 5cm away from a MAP fertilizer site. Sample (1972)determined that adsorption could account for 20% of P retention adjacent to the fertilizer pellet and 60% at a distance of 15mm.

2.2.1.7. Role in soil P cycle

When a P fertilizer is added to soil, a complex sequence of reactions follows. Three zones are generally recognized near a fertilizer granule (Sample et al, 1980). The central zone contains the residue of the P fertilizer. Around this zone the concentrated solution results in the precipitation of P minerals. This zone grades into an outer zone in which concentrations are lower and P reactions are mainly with elements on the surface of soil particles. Therefore, the rate at which the soil P cycle returns to steady state conditions

after fertilizer addition increases as one moves away from the fertilizer zone.

2.2.2. Effect of Management upon the Fate of Fertilizer P

2.2.2.1. Introduction

Many factors are involved in P fertilizer management. However, granule placement and size are the management factors of significance to this study.

2.2.2.2. Uptake Efficiency of P

Most experiments show that the uptake efficiency of added P fertilizer in the first season of application is less than 25% (Barber, 1978). At an application rate of 8.4kg P/ha, Egball and Sander (1988) showed how a particle mass of 0.39 mg resulted in an increase in uptake efficiency from 26 to 47% over a particle size of 20 mg.

2.2.2.3. Placement

P placement has recieved considerable research attention because with time soluble phosphates revert to less available forms and remain immobile in the soil. Four broad objectives are involved in studying fertilizer placement. These are: (i) to enhance the efficient use of fertilizer by the plant, (ii) to prevent or reduce environmental contamination, (iii) to prevent fertilizer salt injury to plants, and (iv) to provide an economical and conveniant operation (Randall et al, 1985). These factors are quite important as they relate to the crop and its rooting pattern, the concentration and closeness of fertilizer to the seed, and the soil test level. (Randall and Hoeft, 1988).

Soil placement methods involve varying the volume of soil that the fertilizer is to react with. As mixing of the fertilizer is restricted to a smaller soil volume, the P levels in the fertilized soil increase. Higher P levels in the fixed soil volume mean the nutrients remain available for a longer period of time. Band placement decreases the soil surface area in contact with added fertilizer with a consequent reduction in the amount of fixation. A possible drawback of smaller soil volumes per mass of fertilizer is that a smaller root mass is responsible for the P uptake. Thus, for maximum fertilizer efficiency, a compromise must be

reached between the soil volume that is fertilized and the root distribution so the probability of root-fertilizer contact is optimized and fixation minimized.

It is generally found, with low fertilizer rates, the efficiency of nutrient uptake is greater for band than broadcast application. For soils with low soil test available P, placement in the effective rooting zone generally results in greater efficiency of P use (Young et al, 1985; Engelstad and Terman, 1980). Slight et al (1984) also concluded that the early beneficial effects of banding are obtained mainly from placing all of the fertilizer P where contact by active roots is likely, so localized placement of fertilizer should be more efficient than broadcast application.

However, banding alone on low P soils is shown to be inadequate and supplementary broadcast P is needed to reach top yields (Barber 1958; Welch et al, 1966b). Wager et al (1985) also found the combination of broadcast and seed placed treatments enhance P uptake.

Plants take up P when it is in solution; in a dry climate seed placed P may not enter solution and thus would not be available to the plant. Harapiak and Beaton (1986) found that under dry conditions, wheat responses are greatest when all of the fertilizer P is deep-banded and smallest when the P is seed placed. The subsoil retains a higher moisture content allowing P to remain in solution longer. McConnel et al (1986) also found deep bands 15cm deep to be the most efficient depth for P fertilizer uptake.

Banding an immobile nutrient such as P generally becomes less important as soil P reserves rise over time. Wager et al (1985) found that a single broadcast application of 40 kg P ha^{-1} increased yields for 5 years and increased average yield and P uptake similar to that of annual seed placed applications of 10 and 20 kg P ha^{-1}. This indicates a single broadcast P application can produce yields comparable to annual seed placed P applications without requiring additional fertilizer inputs.

2.2.2.4. Fertilizer Granule Size

Particle size of P fertilizer granules influences the utilization efficiency of applied P by affecting the distribution of P within the band and by determining the effective surface area of the fertilizer granule.The distribution of fertilizer P within the band, whether continuous or discontinuous, is shown to be an important factor in the efficiency of applied P (Anghinoni and Barber, 1980; Sleight et al, 1984). The effective surface area of a fertilizer granule is related to the reactivity of P with the soil (Kilmer and Webb, 1968).

It is widely recognized that the optimum distribution of P granules has to be weighed against the rate of P fixation. Distribution of pellets within a band influences contact of roots with fertilizer P (Barber, 1974). Nonuniform distribution of fertilizer P within a band affects root contact and thus yield (Stryker, 1974). While it has been shown that the total P needs of a plant can be met by a single root (Kissel and Ragland, 1967), it is desireable to have more roots exposed to available P (Stryer et al, 1974). When fertilizer particles are not placed in a continuous band the number of root fertilizer contacts have to increase to attain the same yield (Eghball and Sander, 1988).

Numerous investigators have reported increases in early crop response with an increase in granule size of water soluble P fertilizers when applied at a low rate to acid soils. For water soluble P fertilizer granules up to 6mm diameter, effectiveness is related to the amount of water soluble P per granule which in turn determines the volume of soil affected by P (Taylor and Terman,1964; Sample and Taylor, 1964). Crop response to larger granules depends on the probability of roots finding the very few diffusion zones at a given rate of P application (Moreno, 1959; van Burg, 1963).

Granulation or banding of calcium phosphates has little or no agronomic advantage for alkaline soils. The local acidification near MAP fertilizer as NH4-N is nitrified may increase availability of P. Solutions, suspensions and solid P fertilizers having similar solubilities and when similarly placed in an alkaline soil at a given P rate, show similar

availability to crops. P solubility effects related to granule size in general tend to be obscured at higher available P levels in soils.

Particle size of P fertilizer significantly affects measured crop parameters only on soils which have the greastest yield increases due to applied P. Sander and Eggball (1988) observed the optimum fertilizer particle size within a band at 8.4kg P/ha to be 0.39mg/particle. Grain yields were lower for smaller size prills because of the larger surface area for reaction with soil constituents which reduces fertilizer P availability. Grain yield was lower for larger prill sizes because root - P fertilizer contact was probably lessened by a discontinuous band. This mid range particle size had an average spacing within the band of only 0.003cm. Sander and Egball (1988) noted that as the rate of P application increased to 16.8 and 23.2 kg/ha the effects of particle size and surface area disappear. It is apparent that yield differences due to P fertilizer particle size were most important on soils low to very low in available P where yield responses to applied P were high.

2.3. OBJECTIVES

The objectives of this thesis were to:

1) Identify the reactions that occur when MAP fertilizer is placed in soil. This objective will be analysed by monitoring the ion concentrations in soil solution before and after the addition of MAP fertilizer. Direct observation of P mineral precipitates formed from added P will be attempted with the use of soil thin sections.

2) Identify the movement of added P through the soil P cycle in the season of application. This objective will be accomplished by monitoring the soil P fractions throughout a 3 month period.

3) Identify how the efficiency of the uptake of added P can be affected the granule size and band placement of MAP fertilizer. This objective will be accomplished by monitoring the uptake of ^{32}P by barley. Organic amendments will also be used in an attempt to reduce the contact of added P with the soil material.

3. MATERIALS AND METHODS

3:1 Soil Properties and Sample Preparation

Soils of the Breton (Orthic Gray Luvisol) series and Paddockwood (Dark Gray Chernozem) association were selected as representative of soils which demonstrate low apparent recoveries of added P. The Breton samples were taken from research plots in NE25-47-4-W5 near Breton, Alberta. The Paddockwood samples were taken from a field in NE31-50-10-W3 northeast of Prince Albert, Saskatchewan. Soils of the Breton series and soils of the Paddockwood association are developed on glacial till parent material. The experimental soil sample for the Breton series was taken from a field which had not recieved P fertilizer for 20 years, whereas the experimental soil sample for the Paddockwood association was taken from a field which has received approximately 15 kg P ha^{-1} for 35 years. Serveral routine analyses were conducted on these experimental soils. Surface samples (Ap horizon) of each of these soils were collected from 0-15cm depth, air dried and passed through a 5mm sieve. Particle size analysis was determined using a pipette method (Day, 1965). pH was measured using both 2:1 $CaCl_2$:soil and 2:1 water:soil ratios (M^cLean, 1982). Organic carbon was determined with a Leco combustion furnace (Nelson and Sommers, 1982). Cation exchange (CEC) analyses were conducted using 1M ammonium acetate (pH 7) for the displacement of exchangeable cations followed by alcohol washing and replacement of exchangeable ammonium with sodium ions (Chapman, 1965). Exchangeable cations (Ca, Mg, Na, K) from the ammonium acetate extraction were determined by atomic absorption (Instrumentation Laboratory) (Baker and Suhr, 1982) and CEC was determined by measuring displaced ammonium with an autoanalyzer (Technicon) (Rhoades, 1982). Extractable aluminum, iron and manganese were determined using both ammonium oxalate (AO) extractant and dithionite-citrate-bicarbonate (DCB) reductant-extractant (McKeague, 1978). The extracted AO and DCB solutions were analysed for Al, Fe

and Mn using an ICP (Department of Chemistry-Spectral Services- University of Alberta). The clay and silt fractions separated during particle size analysis were subjected to X-ray diffraction analysis for minerological determination. The Breton and Paddockwood clay samples were prepared using the paste technique and were subjected to seven pre-treatments to permit a clear identification of the minerals present (De Kimpe, 1978). The x-ray diffractograms were prepared using Cok radiation at 50 kv and 25mA, and at a scan speed of $1^{o}2\theta$ min^{-1}.

3.2 Greenhouse Experiment

During the first part of the experiment plastic pans were set up in the greenhouse to determine the effect of different fertilizer granule sizes and methods of application on P fertilizer uptake by plants of barley (*Hordeum vulgare* L. cv Express) and transformations within the soil. Sieved soil materials were placed in each of the 30cm (length) by 25cm(width) by 20cm (height) pans. Each pan was an experimental unit. MA^{32}P fertilizer bands were placed 2cm below and 2cm to the side of the seed row. The locations of fertilizer granules were marked for identification with plastic toothpicks. In other treatments fertilizer bands were also placed 2cm to theside by 10cm below the seed row. After germination the soil material was wetted regularly to keep the moisture content near field capacity.

There were seven treatments applied, each replicated three times for each of the soils plus three additional treatments replicated three times for the Breton soil only (Table 3.1). The variables in the experiment were fertilizer granule size, fertilizer application location and addition of an organic amendment. MA^{32}P fertilizer was added as a tracer of P uptake by barley. The MAP fertilizer was added at a rate of 20 kg ha^{-1} (or 0.50g MAP pot^{-1}). K_2SO_4 and NH_4NO_3 were added to the soil surface of all treatments at a rate of 20 and 50 kg ha^{-1}, respectively. Thirty barley seeds were added per pot.

TABLE 3.1. Form of fertilizer application, depth of application and nature of organic amendment used in the greenhouse experiment.

Code	Mass of MAP fertilizer granule (g)	Number of granules per pot	Depth of band below seed row(cm)	Carbon source for amendment/ encasement
Control	-	-	-	-
SolutionP	-	-	2	-
$0.01g^{s}$	0.01	50	2	-
$0.10g^{s}$	0.10	5	2	-
$0.50g^{s}$	0.50	1	2	-
$Straw^{s}$	0.10	5	2	Straw
$Peat^{s}$	0.10	5	2	Peat
$0.01g^{d\#}$	0.01	50	10	-
$0.10g^{d\#}$	0.10	5	10	-
$0.50g^{d\#}$	0.50	1	10	-

Indicate treatments applied to Breton soil only.
s,d Indicates the application of MAP fertilizer in shallow and deep bands, respectively.

Plants were harvested at 30, 60 and 90 days by cutting the shoots at ground level. The harvested plant material was dried and weighed. The dried plant material was then acid digested (Olsen and Sommers, 1982) and measurement of ^{32}P uptake was conducted with a scintillation counter.

After the third harvest, soil cores 6cm in diameter were removed for construction of soil thin sections. The soil cores were centered around previously marked fertilizer placements. The soil cores were air-dried in the laboratory, impregnated with epoxy resin and cut into 7 by 5 cm thin sections using procedures described by Brewer and Pawluk (1975).

Soil cores of 2cm diameter were also collected at three lateral distances from the fertilizer placement site(0-1cm, 2-4cm and 5-7cm). Each 2cm diameter core was then divided at the depths 0-2cm, 2-4cm and 4-5cm. The soil material was analysed for organic P content by the ignition method (McKeague, 1978). The soil material was also analysed to determine the distribution of P among soil P fractions using a sequential extraction procedure (O'Halloran et al, 1987).

Soil thin sections were analysed petrographically for soil fabric and for P crystal identification. The thin sections were also mapped for P, Ca, Mg, Mn, Fe, Al and Si on the SEM/EDX to determine the distribution pattern and elemental association of added P. Mean contrast analyses were conducted on 32P uptake and yield data by the General Linear Models program of SAS (1985).

3.3 Equilibration Experiment

The Breton and Paddockwood soil materials were also used in this experiment. MAP fertilizer solution was evenly added to 250g of sieved soil to bring the moisture content to field capacity. Fertilizer rates corresponded to the P levels found within 1cm radius of the 0.10g granule in the greenhouse experiment. The soil materials equilibrated with the MAP in plastic containers (experimental unit) were kept at 25C for three time periods. Deionized

water was added regularly to maintain field capacity. Thus there were four treatments and three time periods each replicated three times (Table 3.2); two of the treatments were not tested with the Paddockwood soil.

The soil pore water was extracted at each time period by immiscible displacement (Barrow, 1982). The following chemical analyses were performed on the pore water extacted by immiscible displacement from the equilibrating soil samples: the cations Ca, Mg, Na, K, Fe, Al, Si and Mn were anlysed by atomic absorption (Baker and Suhr, 1982; Rhoades, 1982); the anions PO_4, SO_4 and NO_3 were analysed by ion chromotography (Dionex); ammonium ion was anlysed by an autoanalyser (Technicon) (Keeney and Nelson, 1982); and electrical conductivity (EC) and pH were analysed with a conductivity meter and an electrode, respectively (Rhoades, 1982). These data were then used to calculate ion activities with the use of the thermodynamic models 'Soil Solution' and 'MINTEQ'. Analytical concentrations of cations and anions together with pH and EC values, all derived from extracted pore water, were used as input parameters for the models. The calculated ion activities were then used to calculate the IAP of the solution species which compose the clay and P minerals of interest. The Ksp of these minerals were calculated separately using thermodynamic data obtained from Rai and Lindsay (1975) and Lindsay (1979). Tables 3.3 and 3.4 show the Ksp values calculated at 25C for selected P and clay minerals considered in this thesis (Rai and Linsay, 1975; Lindsay, 1979). The IAP calculated from modelled ion activities was then compared to the Ksp values for minerals listed in tables 3.3 and 3.4 to obtain the saturation index (SI) value (log IAP/Ksp). $SI<0$, $SI=0$, and $SI>0$ In logarithimic form refer to undersaturated, saturated and supersaturated conditions, respectively, with reference to the minerals in question. The ion activities were also compared to clay mineral and P mineral isoline diagrams. Samples from the same experimental unit also underwent sequential extraction to determine the distribution of soil P among fractions (O'Halloran et al, 1987).

The fractionation procedure was conducted as a split-plot experiment

TABLE 3.2. Concentration of P and equilibration time for P equilibrium studies.

Soil	Equilibrating P concentration (mg P/g soil)	Time	Amount of alfalfa amendment (g)
Breton	0	1 hr	0
	5.2	1 hr	0
	5.2	1 hr	50
	16	1 hr	0
	0	30 days	0
	5.2	30 days	0
	5.2	30 days	50
	16	30 days	0
	0	60 days	0
	5.2	60 days	0
	5.2	60 days	50
	16	60 days	0
Tiller	0	1 hr	
	5.2	1 hr	
	0	30 days	
	5.2	30 days	
	0	60 days	
	5.2	60 days	

TABLE 3.3. Equilibrium constants of relevant clay mineral equilibria.

Reaction		Log K
$KAl_3Si_3O_{10}(OH)_2$(muscovite) + $10H^+$	= $K^+ + 3Al^{3+} + 3H_4SiO_4$	17.08
$Mg_5Al_2Si_3O_{10}(OH)_8$(chlorite) + $16H^+$	= $5Mg^{2+} + 2Al^{3+} + 3H_4SiO_4 + 6H_2O$	72.97
$Al_2SiO_5(OH)_4$(kaolinite) + $6H^+$	= $2Al^{3+} + 2H_4SiO_4 + H_2O$	6.67
$[(Si_{7.87}Al_{0.13})(Al_{3.03}Mg_{0.58}Fe_{0.45})O_{20}(OH)_4]$ (montmorillonite) + 7.48 H2O + $12.52H^+$	= $3.16Al^{+3} + 0.58Mg^{2+} + 0.45Fe^{3+} + 7.87H_4SiO_4$	0.48

Source: Rai and Lindsay, 1975. A Thermodynamic Model for Predicting the Formation, Stability, and Weathering of Common Soil Minerals. Soil Science Society of America Proceedings, Vol. 39, p.991-996.

TABLE 3.4. Equilibrium constants of relevant phosphate mineral equilibria.

Reaction		Log K
$AlPO_4 \cdot 2H_2O$(variscite) + $2H^+$	= $Al^{+3} + H_2PO_4^- + 2H_2O$	-2.50
$FePO_4$ + $2H^+$	= $Fe^{3+} + H_2PO_4^-$	-5.37
$FePO_4 \cdot 2H_2O$(strengite) + $2H^+$	= Fe3+ + H_2PO_4- + $2H_2O$	-6.85
$CaHPO_4 \cdot 2H_2O$(brushite) + $2H_2O$ + H^+	= $Ca^{2+} + H_2PO_4^-$ + 2H2O	0.63
$CaH(PO_4)_3 \cdot 2.5H_2O$(octacalcium phosphate) + $5H^+$	= $4Ca^{2+} + H_2PO_4^-$ + $2.5H_2O$	11.76
$Ca_3(PO_4)_2$(tricalcium phosphate) + $4H^+$	= $3Ca^{2+} + 2H_2PO_4^-$	10.18
$Ca_5(PO_4)OH$(hydroxyapatite) + $7H^+$	= $5Ca^{2+} + 3H_2PO_4^- + H_2O$	14.46
$MgHPO_4 \cdot 3H_2O$(newberryite) + H^+	= Mg^{2+} + H_2PO_4- + $3H_2O$	1.38
$MgNH_4PO_4.6H_2O$(struvite) + $2H^+$	= $Mg^{2+} + NH^{4+} + H_2PO_4^-$ + $6H_2O$	6.40

Source: Lindsay, 1979. Chemical Equilibria.

(Dr. Hardin, Dept. of Animal Science, University of Alberta, 1990, personal communication), and the pore water data was analysed as a two way anova. The analyses were conducted by the General Linear Models program of SAS (1985).

4. Discussion

4.1 Soil Characteristics

4.1.1 Introduction

Both the Breton and Paddockwood soils were developed on glacial till parent materials. However, the geographical distance between sites suggests the glacial till parent materials probably originated from different bedrock formations. The geographical location of the two soils, on the fringes of the boreal forest, would generate similar environmental conditions responsible for soil formation. The soil properties reflecting from the parent material and environmental conditions can greatly affect the way added P reacts with the soil.

4.1.2 Soil Minerology

The minerology of the clay and silt fractions of the two soils is very similar (Table 4.1, Appendix I). Smectite is the dominant clay mineral of both soils. The minerology of the clay and silt fractions is similar dispite the distance between the two sampling sites.

The most important characteristics of the minerology of the soil clay fraction that relate to added P are the ion exchange porperties. The ion exchange properties of soil clays vary with the mineral crystal structure. Smectite minerals have a large CEC of approximately 110 cmol (+) kg-1 (Borchardt, 1977). This high CEC is a result of the dominant pH-independent charge associated with smectite minerals. The exchange complex of smectite minerals allows most monovalent and divalent cations to be completely exchangeable at all pH values. A list of the mechanisms involved in the exchange reactions of smectite minerals is outlined in Table 4.2.

Mica has a low CEC relative to smectite clay minerals because the interlayer cations

TABLE 4.1. Minerology of the clay (<2μm) and silt (2-20 μm) fractions of the Paddockwood and Breton soils.

Soil	Fraction	Minerology in order of decreasing abundance
Paddockwood	Clay	Smectite, mica, kaolinite, quartz, chlorite
	Silt	Quartz, feldspar
Breton	Clay	Smectite, mica, kaolinte, quartz, chlorite
	Silt	Quartz feldspar

TABLE 4.2. Reactions of various elements with smectites in soil environments.

Element	Type of Reaction
Ca^{2+}, K^{+}, NH_4^{+}	Cation exchange
H_3O^{+}	Cation exchange, replaces octahedral Al
Na^{+}	Cation exchange, replaced from exchange by octahedral Mg and Al
Fe^{3+}	Cation exchange, hydrolysis, and dissolution of smectite
Al^{3+}, Mg^{2+}, Fe^{3+}	Cation exchange, hydroxy interlayer formation
$H_2PO_4^{-}$	Anion exchange

Source: Borchardt, 1977. Montmorillonite and Smectite Minerals IN Minerals in Soil Environments. Dixon Ed. ASA. Madison Wisconsin.

are not exchangeable. Potassium dominates the interlayer region and is released slowly through selective exchange with other monovalent ions such as ammonium (Fanning and Karamides, 1977).

Kaolinite also has a low CEC relative to smectite clay minerals. The low CEC of kaolinite is a result of low pH independent - permanent negative charge and substantial pH dependent charge. Therefore, kaolinite minerals have ion exchange properties similar to amorphous and oxide minerals. Despite the low CEC, exchangeable sodium may be retained in kaolinite mineral structure under acid conditions (Dixon, 1977).

Soil extraction with A.O. and D.C.B. (Table 4.3) indicate the presence of oxides of Al, Fe and Mn within the soil matrix. Iron and manganese nodules within the soil matrix were also detected on soil thin sections (Plate 4.1).

Plate 4.1: EDX maps of sesquioxidic nodules in the Paddockwood sample: a) the nodules are composed of iron and manganese oxides; b) P is not associated with the surface of the nodule.

4.1.3 General Analytical Properties of Experimental Soils

In addition to having similar minerology in the silt and clay fractions, the two experimental soils have similar particle size distributions (Table 4.4). The Paddockwood soil has a loam texture and the Breton soil has a silty loam texture. Therefore, based on clay minerology and particle size distribution the two experimental soils should have similar CEC values.

Actual measurements of CEC and exchangeable cations for the two experimental soils are also presented in Table 4.4. The Paddockwood sample has a higher CEC (20 cmol(+) kg^{-1}) than the Breton sample (14.5 cmol(+) kg^{-1}), and it also has higher exchangeable calcium and magnesium values than the Breton sample.

The Breton samples have much higher values of DCB and AO extractable Al, Fe and Mn than the Paddockwood samples. The Paddockwood sample has higher organic carbon content and pH values than the Breton sample (Table 4.4). Therefore, some soil properties

TABLE 4.3. Extractable Fe, Al and Mn of Experimental Soils.

Treatment	Al	Fe	Mn
		%	
		PADDOCKWOOD	
DCB	0.067	0.42	0.029
AO	0.086	0.24	0.029
		BRETON	
DCB	0.10	0.62	0.066
AO	0.13	0.44	0.080

Plate 4.1. EdX maps of sesquioxidic nodules in the Paddockwood sample: (a) the nodules are composed of iron and manganese oxides; (b) P is not associated with the surface of the nodule

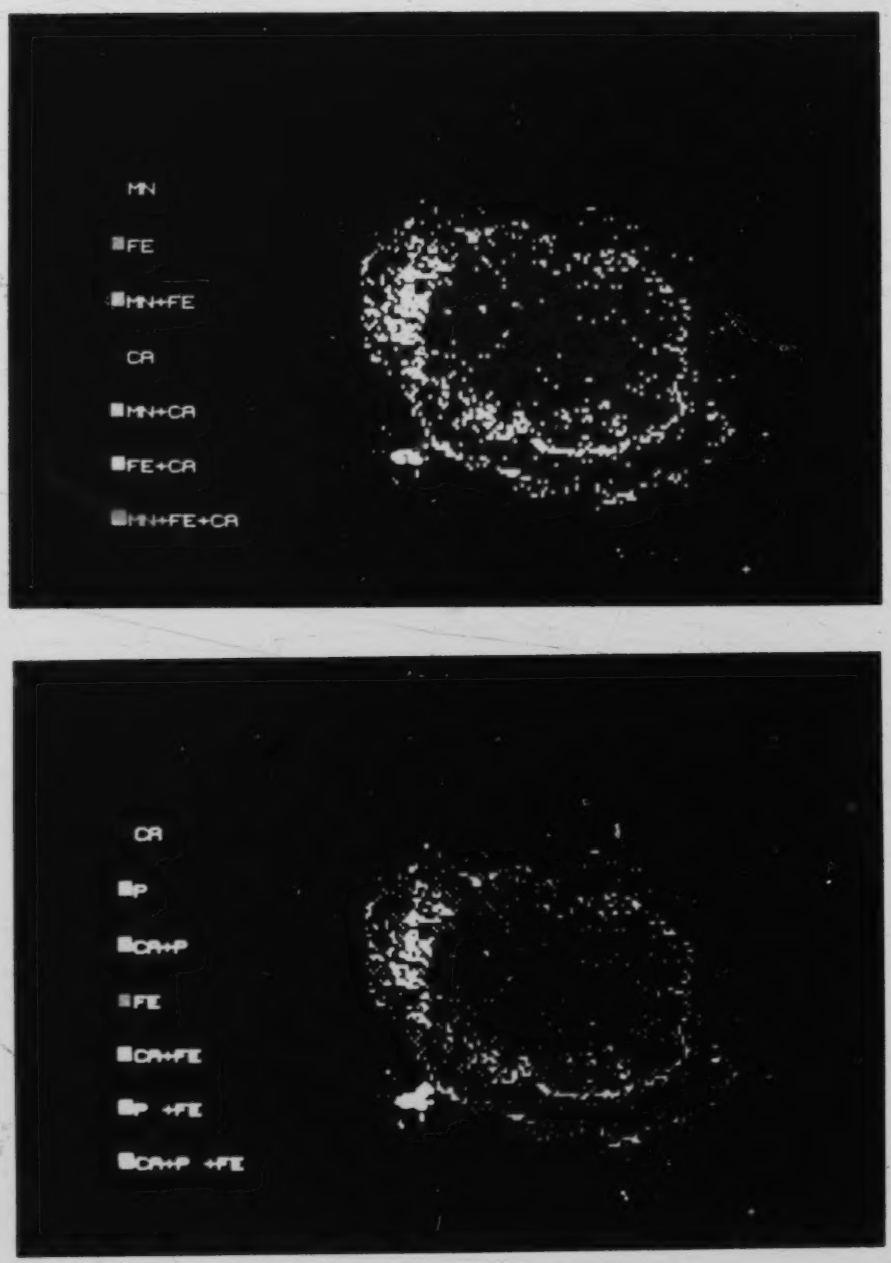


TABLE 4.4. Chemical properties of experimental soils.

Soil	pH		OC	Exchangeable Cations				CEC	Particle size distribution		
	$CaCl_2$	HOH		Ca	Mg	K	Na		Sand	Silt	Clay
			%	cmol(+) kg^{-1}					%		
Paddockwood	6.5	6.8	3.4	20.9	2.8	0.37	0.41	20.0	38	45	17
Breton	5.4	5.8	1.4	12.3	1.2	0.29	0.45	14.5	35	51	14

are very contrasting between the two experimental soils.

The fertilizer history of the two soils previous to the time of sampling is quite different. The application of 15 kg P ha^{-1} annually to the Paddockwood sample site for the 35 years prior to sampling is in contrast to the Breton sample site which had no fertilizer addition during the same time period.

4.1.4. Soil Solution Characteristics

Breton and Paddockwood samples were equilibrated at field capacity. The pore water was extracted after equilibration periods of one hour, one month and two months. The soil solution was then analysed for a suite of ion concentrations.

The cations Ca^{2+}, Mg^{2+} and Na^{+} steadily increase and then stabilize with time while the remaining suite of cations maintain their original soil solution concentration through a two month period (Table 4.5 and 4.6). The concentrations of Ca^{2+}, Mg^{2+} and Na^{+} increased at the same relative rate and then stabilized near the same relative concentrations.

The increase and subsequent stabilization of Ca^{+2}, Mg^{+2} and Na^{+} ion concentrations may be the result of their dominance on the exchange complex of the two experimental soils (Tables 4.5 and 4.6). Therefore, their ion concentration in soil solution is a reflection of the equilibrium relationship between the soil solution and the exchange complex. We can then use these equilibrium values to determine the effect of MAP fertilizer addition to soil.

4.2. Characteristics of the Reaction Between Soil and Fertilizer in Solution

Breton and Paddockwood samples were also equilibrated at field capacity after the addition of 5.2 (low rate) and 16 mg P/g soil (high rate) of MAP fertilizer. The pore water was extracted after equilibration periods of one hour,

one month and two months. The soil solution was then analysed for a suite of ion concentrations.

TABLE 4.5. Ion concentration means of Breton soil pore water equilibrated at field capacity with three different phosphate addition levels for up to two months.

	Concentration of P in equilibating soil, mg P/g soil												
	0			5.2			16			5.2 + Alfalfa			
	Equilibrating Time, days												
ION	1hr	30	60	1hr	30	60	1hr	30	60	1hr	30	60	LSD (0.05)#
pH	6.0	6.3	6.4	4.1	5.1	5.5	4.1	5.0	5.2	4.6	7.6	5.0	0.17
EC (dS/m)	2.0	2.0	3.20	13	6	5.6	15	15	15	12	9	9	6.1
Ca (mmol/L)	16	24	27	91	7.2	4.6	100	4.7	5.0	-	27	3.4	7.43
Mg (mmol/L)	3.5	5.1	6.1	30	6.4	4.7	40	60	60	-	20	0.37	3.73
K (mmol/L)	0.33	0.26	0.31	2	1.1	0.87	5.7	3.1	3.8	-	31	20	2.14
Na (mmol/L)	2.7	3.1	3.6	6.2	3.3	3.2	6.9	4.8	5.3	-	6.6	4.7	0.44
Fe (μmol/L)	9.0	6.0	6.0	54	20	14	160	197	209	322	36	260	36
Mn (μmol/L)	36	18	18	460	200	150	2300	910	150	1100	930	82	232
Al (μmol/L)	1.9	2.6	3.3	410	10	4.5	740	670	440	10	7	6	20
Si (mmol/L)	1.1	1.1	2.1	13	5.3	4.0	15	3.7	3.9	12	4.9	0.68	0.68
NH_4(mmol/L)	0.27	0.24	0.28	280	100	93	1300	1600	1900	230	120	120	30.8
PO_4(mmol/L)	0	0	0.032	570	110	61	1600	1600	1500	290	23	20	52.8
SO_4(mmol/L)	0.46	0.49	0.44	1.5	5.6	3.4	1.7	3.6	3.6	6.6	6.0	7.7	1.5
NO_3(mmol/L)	34	34	33	33	32	36	32	32	32	32	110	36	4.0

LSD (0.05) = least significant difference between the treatment means at the 0.05 probability level.

TABLE 4.5. (continued). Analysis of variance for the Breton sample treatments.

Source	df	pH	EC	Ca	Mg	K	Na	Fe	Mn	Al	Si	NH4	PO4	SO4	NO3
Time	2	***	*	***	*	***	***	***	***	ns	***	***	***	**	***
Conc	3	***	***	***	***	***	***	***	***	***	***	***	***	***	***
Time*Conc	6	***	***	***	***	***	***	***	***	ns	***	***	***	ns	***
Error	24														

The difference between means is significant at: ns, not significant; *, adjusted $p < 0.05$; **, adjusted $p < 0.01$; *** adjusted $p < 0.001$.

TABLE 4.6. Ion concentration means of Paddockwood and Breton soil pore water equilibrated at field capacity with added MAP fertilizer for up to two months.

	Concentration of P in equilibrating soil (mg P/g soil)													
	Control			5.2			Control			5.2				
	Equilibrating Time (days)													
Ion	1hr	30	60	1 hr	30	60	1 hr	30	60	1 hr	30	60	LSD1 0.05	LSD2 0.05
	PADDOCKWOOD						BRETON							
pH	6.8	6.9	6.8	4.5	5.2	5.3	6.0	6.3	6.4	4.1	5.1	5.5	0.04	0.04
EC (dS/m)	1.6	1.9	2.2	10	6.7	6.7	2.0	2.0	3.2	13	6	5.6	0.2	0.23
Ca (mmol/L)	10	14	16	44	8.9	8.1	16	24	27	91	7.2	4.6	1.7	2.5
Mg (mmol/L)	4.9	7.0	7.8	40	14	13	3.5	5.1	6.1	30	6.4	4.7	2.2	1.5
K (mmol/L)	0.43	0.36	0.46	4.8	2.6	2.7	0.33	0.26	0.31	2	1.1	0.87	0.07	0.05
Na (mmol/L)	1.6	1.9	2.3	3.6	2.7	3.0	2.7	3.1	3.6	6.2	3.3	3.2	0.10	0.16
Fe (µmol/L)	7.2	3.6	3.6	45	23	16	9.0	6.0	6.0	54	20	14	1.47	0.79
Mn (µmol/L)	1.8	0	0	270	250	220	36	18	18	460	200	150	0.0	2.66
Al (µmol/L)	1.1	1.8	2.3	30	6.0	4.4	1.9	2.6	3.3	410	10	4.5	n/a	0.02
Si (mmol/L)	0.46	0.64	0.85	10	4.3	3.6	1.1	1.1	2.1	13	5.3	4.0	0.02	0.17
NH_4 (mmol/L)	0.19	0.55	0.33	150	120	120	0.27	0.24	0.28	280	100	93	71	39.2
PO_4 (mmol/L)	0	0	0	360	280	130	0	0	0.032	570	110	61	32	41
SO_4 (mmol/L)	1.2	0.97	1.2	2.7	1.7	3.0	0.46	0.49	0.44	1.5	5.6	3.4	0.93	1.11
NO_3 (mmol/L)	30	33	36	32	32	34	34	34	33	33	32	36	8.4	4.5

LSD1 (0.05) = least significant difference between the treatment means at the 0.05 probability level within the Paddockwood sample treatments.

LSD2 (0.05) = least significant difference between the treatment means at the 0.05 probability level between the Paddockwood and Breton sample treatments.

TABLE 4.6 (continued). Analysis of variance for the Paddockwood sample treatments.

Source	df	pH	EC	Ca	Mg	K	Na	Fe	Mn	Al	Si	NH4	PO4	SO4	NO3
Time	2	***	***	***	***	***	***	*	**	**	***	ns	***	ns	ns
Conc	1	***	***	***	***	***	***	***	**	**	*	***	***	**	**
Time*Conc	2	***	***	***	***	***	***	*	**	**	***	ns	***	ns	*
Error	24														

The difference between means is significant at: ns, not significant; *, adjusted $p<0.05$; **, adjusted $p<0.01$; *** adjusted $p<0.001$.

TABLE 4.6 (continued). Analysis of variance between the Paddockwood and Breton sample treatments.

Source	df	pH	EC	Ca	Mg	K	Na	Fe	Mn	Al	Si	NH4	PO4	SO4	NO3
Soil	1	***	*	***	***	***	***	***	***	***	***	ns	ns	ns	***
Time	2	***	*	***	***	***	***	***	***	***	***	*	***	ns	***
Soil*Time	2	***	ns	***	ns	***	***	***	***	***	***	ns	***	*	***
Conc	1	***	***	***	***	***	***	***	***	***	***	***	***	***	***
Time*Conc	2	***	***	***	***	***	***	***	***	***	***	**	***	ns	***
Soil*Conc	1	***	***	*	***	***	ns	***	***	***	***	ns	ns	ns	ns
Soil*Time* Conc	2	**	ns	***	ns	***	***	***	***	***	***	ns	***	ns	***
Error	24														

The difference between means is significant at: ns, not significant; *, adjusted $p<0.05$; **, adjusted $p<0.01$; *** adjusted $p<0.001$.

4.2.1 Solution Semi-Saturated with MAP Fertilizer

The characteristics of a solution saturated with MAP fertilizer are presented in Table 4.7. The pH of a solution saturated with MAP fertilizer is 3.5 when equilibrium with the dissolution constant of $H_2PO_4^-$ is attained with an initial concentration of 2.9 M. The pore water extracted from the experimental soils one hour after the application of the low rate of P fertilizer (Tables 4.5 and 4.6) has characteristics similar to the solution saturated with MAP fertilizer. The pH of the extracted pore water (Tables 4.5 and 4.6) was slightly higher and the PO_4 and NH_4 concentrations were lower than the solution saturated with MAP fertilizer.

4.2.2. Flush of Ions into Soil Solution

The addition of MAP to soil caused a unique and consistent change in the ionic concentrations in the soil pore water. The EC of soil pore water dramatically increased with the addition of MAP fertilizer (Tables 4.5 and 4.6). The increase in EC of the pore water reflected increases in the ion concentration of all elements in addition to the components of the fertilizer solution, ammonium and phosphate. One hour after the addition of the low rate of MAP fertilizer the ion concentrations were generally two to three times higher than in the control soil solution (Tables 4.5 and 4.6). The ion concentrations of the basic cations and silica were slightly higher after the high rate of addition of MAP fertilizer. However, the ion concentrations of iron, manganese and aluminum were substantially higher after the addition of MAP fertilizer at the high rate as compared to the low rate (Table 4.5).

Both components of MAP fertilizer solution, ammonium and phosphate, decrease to similar levels at different relative rates after their addition to the soil. One hour after addition, ammonium ion concentration was approximately one half of the phosphate ion concentration. This rapid decrease in ammonium ion concentration coincides with the ion flush into soil solution after the addition of MAP fertilizer. The ammonium ion saturates the exchange complex, decreasing its soil solution concentration, and then releases the

TABLE 4.7. Characteristics of Saturated MAP Fertilizer Solution

Property	MAP Solution Value
pH	3.5
PO_4 (mol/L)	2.9
NH_4 (mol/L)	2.9

Source: Sample et al., IN Khasawneh et al., Eds., The Role of Phosphorus in Agriculture, p. 275. Madison, Wis.; ASA, 1980.

exchangeable cations into solution.

4.2.3. Change in Ion Concentration with Time After the Addition of MAP Fertilizer

One month after the addition of MAP fertilizer at the low rate the EC of the soil solutions decreased to and levelled off around 6 dS m^{-1}. The decrease in EC reflected decreases in concentrations of all ions except sulfate.

Calcium and magnesium show the greatest relative decrease in cation concentration with time after the initial flush caused by the addition of MAP fertilizer at the low rate (Tables 4.5 and 4.6). These two ions reach an equilibrium concentration which is below the control equilibrium concentration (Tables 4.5 and 4.6). The remainder of the cations in soil solution decrease to the level of concentration attained for the control treatment at equilibrium.

After the high rate of MAP fertilizer was added to the soil, the soil solution was dominated by ammonium and phosphate to such and extent that only minor changes in ion concentration occur after their initial flush into soil solution. However, calcium and manganese, in contrast to the remainder of the suite of ions analysed, had quite large decreases in ion concentration from the time of MAP fertilizer addition to a time of one month.

4.2.4 Change in Ion Concentration with Time After the Addition of MAP Fertilizer to Soil with Alfalfa Amendment

When MAP fertilizer was added to soil containing an alfalfa amendment many characteristics of the soil solution were different than when MAP fertilizer was added to the soil without the alfalfa amendment. With most soil solution parameters, the difference between the alfalfa and non-alfalfa treatments occur with the 30 day treatment.

The pH values of the alfalfa treatment immediately after the addition of MAP fertilizer are similar to the non-alfalfa treatment. The pH values between the two treatments are also quite similar after two months of equilibration. However, after one month of

equilibration the pH values of the alfalfa treatment after the addition of MAP fertilizer are two whole units higher than at 2 months (Table 4.4).

Soil solution values of calcium and magnesium are three to four times higher in the alfalfa treatment than in the non-alfalfa treatment one month after the addition of MAP fertilizer. The soil solution values of calcium and magnesium are similar for the two treatments two months after the addition of MAP fertilizer (Table 4.4).

Soil solution values of potassium are higher in the alfalfa treatment than in the non-alfalfa treatment one and two months after the addition of MAP fertilizer. Whereas sodium values are similar between treatments one and two months after the addition of MAP fertilizer (Table 4.4).

Soil solution values of iron and manganese are very high both one hour and two months after the addition of MAP fertilizer to the alfalfa treatment. The soil solution values for iron and manganese one month after MAP addition are similar between alfalfa and non-alfalfa treatments (Table 4.4).

Phosphate values in soil solution are reduced much faster in the alfalfa treatment than in the non-alfalfa treatment. One hour after the addition of MAP fertilizer the phosphate level in soil solution of the alfalfa treatment was half that of the non-alfalfa treatment (Tables 4.5 and 4.6). Also, the phosphate level in soil solution was lower in the alfalfa treatment than in the non-alfalfa treatment two months after MAP addition.

The nitrate levels detected in soil solution were very high one month after the addition of MAP fertilizer to the alfalfa amendment. The nitrate levels in soil solution were similar between alfalfa and non-alfalfa treatments one hour and 60 days after the addition of MAP fertilizer.

The color of the pore water after passing through 0.2μm filters were quite different. The pore water from the control, with no MAP added was clear. The pore water from the soil after MAP was added was clear but yellow (10Y 6/6). The pore water from the soil after MAP was added with an alfalfa amendment was blackish brown (10YR 2/1) and

yellow, clear (10Y 6/6) after one and two months of equilibration, respectively.

4.3. Discussion of the Reaction Between Soil and MAP Fertilizer in Solution

Many researchers have detected a flush of soil cations into solution after the addition of MAP fertilizer (Lindsay et al., 1962; Racz and Soper, 1967; and Bell and Black, 1970a). Similar results have been detected here (Tables 4.5 and 4.6). The possible sources for this flush of ions are from the exchange complex, from oxides, oxyhydroxides and amorphous minerals, and from secondary clay minerals.

4.3.1. Characteristics of Solution Containing MAP Fertilizer Responsible for the Flush of Ions into Soil Solution

The low pH of solutions containing MAP fertilizer, when reacting with soil constituents, affects many properties. Increased ion solubility resulting from fertilizer induced acidification leads to the destabilization of soil minerals and soil organic matter. The soil as a complete unit may not be greatly affected by the low pH due to the buffering capacity of clays and organic matter (Barrow and Shaw, 1976). However, within the vicinity of solutions containing MAP fertilizer, the low pH has a great influence on soil properties which may greatly affect the fate of added P.

In addition to low pH, the high concentration of ammonium ion in the solutions containing MAP fertilizer reacts with the soil constituents. The ammonium ion has a relatively low hydration energy resulting in easy dehydration and strong retention by 2:1 clay minerals (Bohn et al, 1987). Therefore, the high concentration of ammonium ion in solution will tend to replace exchangeable cations on the exchange complex. This may partially explain the increase in EC and ion concentrations after the addition of MAP fertilizer (Tables 4.5 and 4.6). Analytical methods for cation exchange capacity determination such as ammonium acetate saturation ($pH > 7.0$) use high ammonium ion concentrations, similar to those found in the fertilizer treatments, for replacing other ions on the exchange complex.

The ammonium ions in solutions containing MAP fertilizer will affect the exchangeable cations on the exchange complex in a similar manner.

The most probable mechanism of cation exchange with high ammonium levels present in soil solutions containing MAP fertilizer is mass action. The exchange reactions move to completion as the ammonium ions are adsorbed onto the exchange complex thus releasing the exchangeable ions into solution.

4.3.2. Effect of Fertilizer Ammonium on the Soil Exchangeable Cations

Earlier discussion noted the clay minerology of both experimental soils is dominated by smectite. Smectite clay minerals have high CEC properties with pH-independent charge. The high exchange properties of ammonium would cause the ions on the exchange complex to be replaced with added fertilizer ammonium. Therefore, the exchange complex of smectite clay mineral may be expected to be the major source for cations entering soil solution.

An example may indicate the amount of exchangeable cation that could be released into soil solution through exchange with fertilizer ammonium. If the clay fraction contains 80% smectite and has a 20% moisture content, ion exchange can account for an increase of 400 mmol Ca L^{-1} or 800 meq L^{-1}. Therefore, ion exchange from soil clay smectites can fully account for the ion concentrations found in extracted pore water before and after the addition of MAP fertilizer (Tables 4.5 and 4.6).

The exchange complex of the other clay minerals can also release cations into soil solution through exchange with ammonium. The lower CEC and pH-dependent charge of mica and kaolinite minerals, in addition to their lower content in the soil clay fraction, reduces the effect ammonium exchange has on releasing their adsorbed cations into soil solution. The change in pH-dependent charge on the exchange complex of oxide and hydroxide soil minerals, brought about by the decrease in soil pH through the addition of MAP fertilizer, may also result in the release of cations into soil solution.

4.3.3 Effect of the pH of Solution Containing MAP Fertilizer on the Solubility of Soil Minerals

The low pH of solution containing MAP fertilizer increases the solubility of soil minerals. The increased solubility of soil minerals with the addition of MAP fertilizer may release ions into soil solution, by affecting both the exchange complex and the structure of the mineral surface. The solubilities of the soil minerals are different from each other and are important in affecting the release of ions into solution.

4.3.3.1. Oxide and Hydroxide Minerals

Oxide and hydroxide minerals, in addition to their exchange complex, may release ions into soil solution through their dissolution. After the addition of MAP fertilizer, the pH of the soil solution decreases, causing the solubility of oxide and hydroxide minerals to increase (Acquade and Tinsley, 1965; Schwertmann and Taylor, 1977). Therefore, the low pH conditions of the soil solution containing MAP fertilizer, may cause oxide and hydroxide minerals to be sources for aluminum, iron and manganese ions.

Oxide and hydroxide minerals amount to less than one per cent (mass) of the experimental soils (Table 4.1). However, the amount of Al, Fe and Mn in soil solution after the addition of MAP fertilizer is extremely low compared to the amount extracted from the soil by AO and DCB.

4.3.3.2 Clay Minerals

The solubility of secondary clay minerals is also affected by changes in pH. The equilibrium solubility status of clay minerals can be determined from soil solution data. Figures 4.1 to 4.4 depict an increase in the solubility of clay minerals after the addition of MAP fertilizer. The increase in Al concentration associated with the clay mineral isolines of Figures 4.2 and 4.4 after the addition of MAP fertilizer portray the clay mineral response to decreasing pH. One hour after the addition of MAP fertilizer, the soil solution appears to be

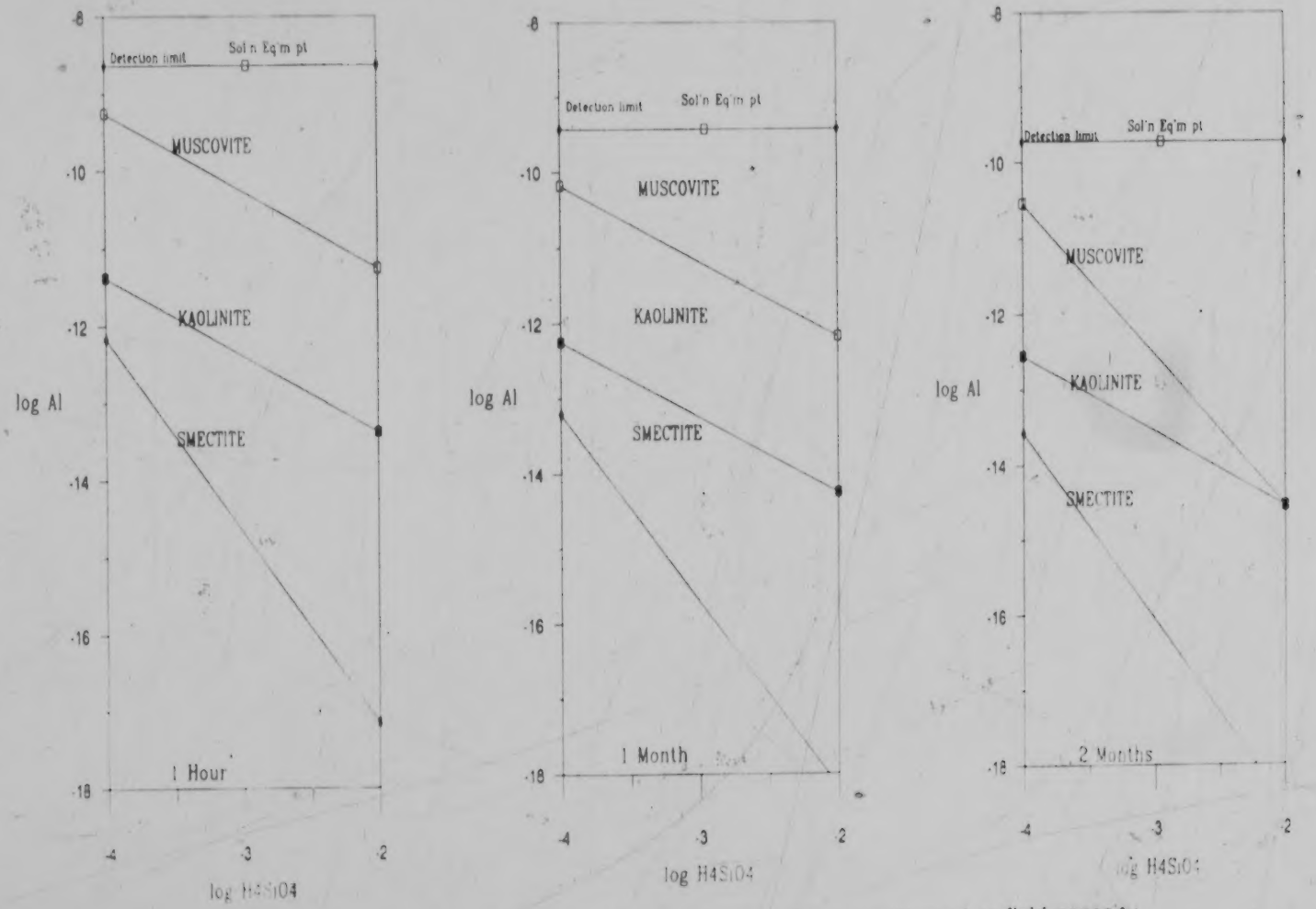


Figure 4.1. Clay mineral solubility diagrams for Breton sample equilibrated at field capacity of up to two months.

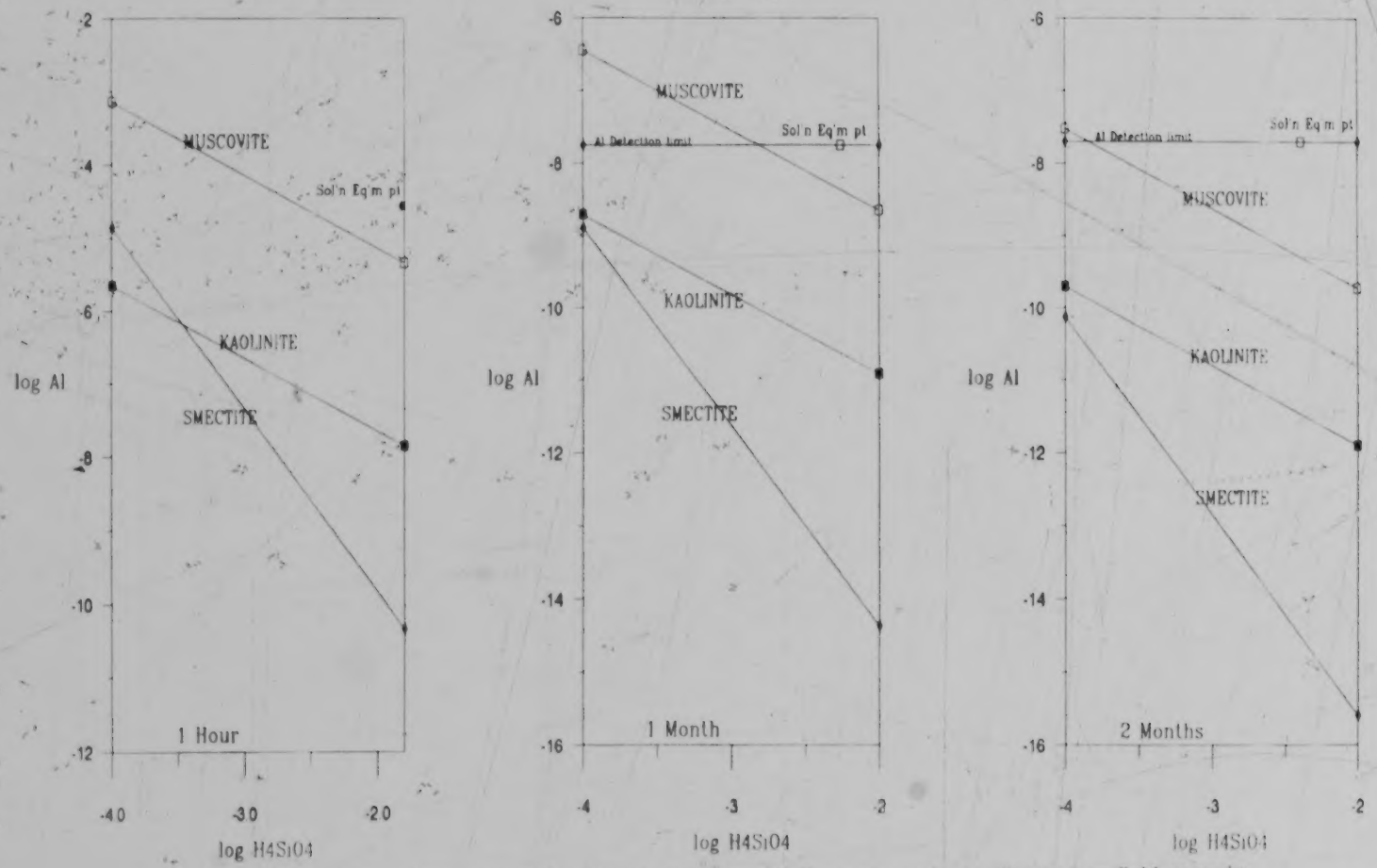


Figure 4.2. Clay mineral solubility diagrams for Breton sample equilibrated at field capacity with the addition 5mg P/g soil for up to two months.

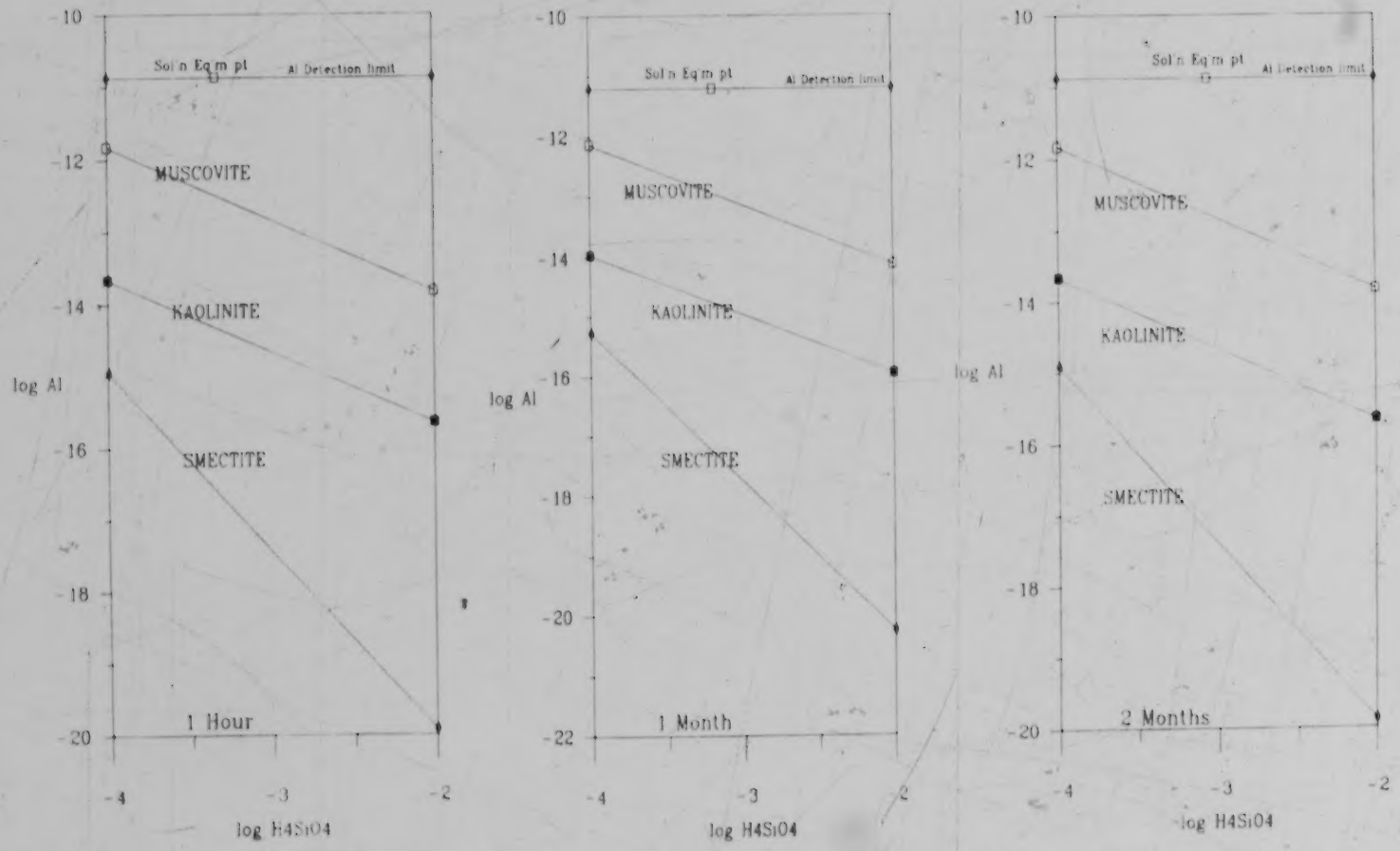


Figure 4.3. Clay mineral solubility diagrams for Paddockwood sample equilibrated at field capacity of up to two months.

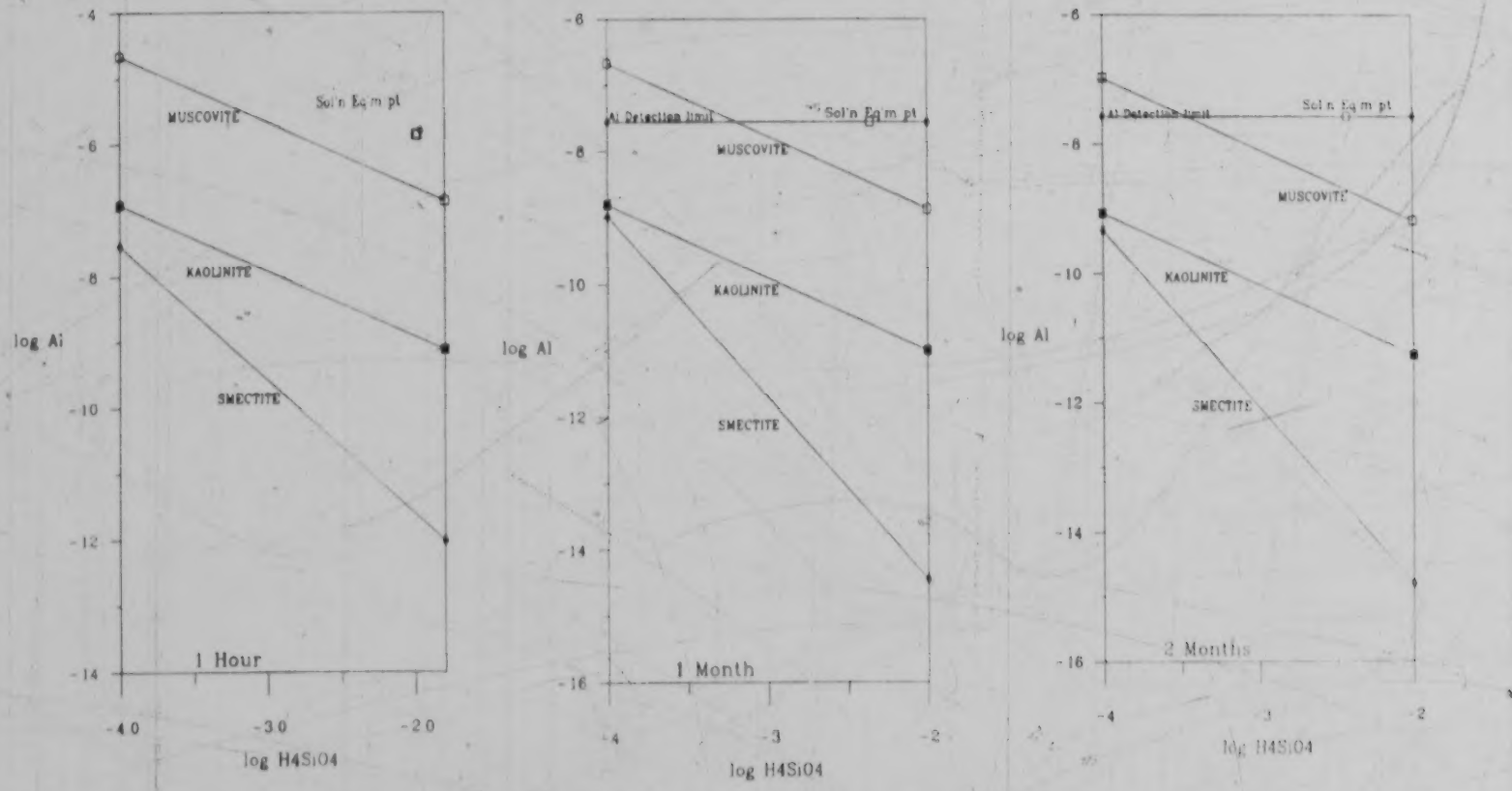


Figure 4.4. Clay mineral solubility diagrams for Paddockwood sample equilibrated at field capacity with the addition 5mg P/g soil for up to two months.

in equilibrium with muscovite, the most soluble clay mineral present (Figures 4.2a and 4.4a). The low Al ion concentration, undetected in all other pore water extractions both before and after the addition of MAP fertilizer, prevents the identification of the soil mineral phase in equilibrium with soil solution at that point in time.

Al, Si, Fe, Mg, Na, O, H and K concentrations are directly affected by changes in the solubility of clay minerals in the Breton and Paddockwood samples. The ions associated with the mineral edges of muscovite are the most directly affected by increased solubility of clay minerals. The ionic concentrations of Si, Fe, and Mn would also be in equilibrium with the soil clay minerals, however, we are unable to determine which clay mineral is in equilibrium with soil solution.

Exchangeable cations and ion complexation properties are indirectly affected by increased solubility of clay minerals. The exchangeable cations are the first to go into solution because they are retained at the surface of clay minerals. The exchange complex was previously discussed as the major source of exchangeable cations. As the exchangeable ions move into solution they undergo complexation reactions with other ions. Therefore, even if the dissolution of clay minerals does not contribute a high concentration of ions to soil solution directly from the lattice structure, it does indirectly affect exchangeable cation concentration and ion complexation reactions.

4.3.4. Sinks of Added Phosphorus with Time after the Addition of MAP Fertilizer

The large decrease in phosphate ion concentration in soil solution from one hour to two months after the addition of the low rate of MAP fertilizer is the result of a complex set of reactions. Soil solution phosphate can be tied up in an array of P mineral precipitation and P adsorption reactions.

4.3.4.1 Relation of Soil Solution Phosphate and Calcium/Magnesium with Time

Ions in soil solution decrease in concentration from one hour to one month after the addition of MAP fertilizer. The ion concentrations have appeared to stabilize somewhat by the end of the first month after the low level of MAP addition. Two cations, calcium and magnesium decrease in concentration to levels lower than the control treatment whereas all other ion concentrations decrease to levels slightly higher than the control treatment (Tables 4.5 and 4.6). The exchangeable cations would be expected to have higher concentrations after the addition of MAP fertilizer than prior to the addition of MAP fertilizer; assuming the exchange complex would become dominated by fertilizer ammonium. Therefore, there must be some additional reaction occurring that removes these two cations from solution.

Phosphate has the largest decrease in ionic concentration in soil solution from one hour to one month after the addition of MAP fertilizer (Tables 4.5 and 4.6). The decrease in calcium ion concentration in soil solution coincides with the decrease in soil solution phosphate ion concentration. The decrease in calcium in soil solution despite an exchange complex saturated with ammonium, suggests that calcium and phosphate may be precipitating to form calcium phosphate minerals. The decrease in calcium ion also provides an indication of the amount of P mineral formation taking place. With a decrease of 86 mmol Ca L^{-1} from one hour to two months after the addition of the low rate of MAP fertilizer (Tables 4.5 and 4.6), about 43 mmol PO4 L^{-1} could be tied up as dicalcium phosphate.

4.3.4.2 Relation of Soil Solution Phosphate with Iron, Aluminium and Manganese Over Time

After the initial ion flush resulting from the addition of MAP fertilizer, the ions Fe, Mn, Al and Si also decreased in concentration (Tables 4.5 and 4.6) resulting from their decreased solubility at pH values above 5 (Acquage and Tinsley, 1965). Therefore, one may

anticipate the formation of aluminosilicate minerals. Unfortunately, the exceedingly low level of Al ion concentration does not allow us to observe if the clay minerals are supersaturated.

Fe, Al, Mn and Si ions could also be precipitating as oxide coats on surfaces of pre-existing soil minerals. Amorphous silica accumulates as an intermediate in supersaturated solutions because it precipitates more readily than crystalline silica (Wilding et al, 1977). As can be seen from the clay mineral solubility diagrams (Figures 4.1 to 4.4), the silica activity in soil solution moves towards amorphous silica equilibrium (pH_4SiO_4 = 3.1) supporting the possibility that amorphous silica components are forming.

Although ferrihydrite will form quickly if its reasonably high solubility product is exceeded, geothite is more likely to form at pH levels present in the fertilized soil solutions. Geothite formation is faster and its proportion increases as the pH of the solution decreases from 7 to 4 (Schwertmann and Taylor, 1977).

The decrease in Fe, Al and Mn concentrations in soil solution after the addition of MAP fertilizer could be explained by the precipitation of Fe, Al and Mn phosphate minerals in addition to the precipitation of alumininosilicate minerals. The decrease in ion concentrations of Fe, Al and Mn in the soil solution from one hour to one month after the addition of MAP fertilizer is very low in comparison to the decrease in Ca ion concentration for the same time period. This may lead one to assume that only a small amount of phosphate is reacting with Fe, Al and Mn. However, the extraction of pore water is a static measurement that cannot determine soil solution dynamics. Therefore, Fe, Al and Mn may be continually released into soil solution with immediate reaction with added phosphate. Soil solution dynamics such as these would not be detected with pore water extraction. The maintanence of high concentrations of Fe, Al and Mn in soil solution after the addition of the high rate of MAP fertilizer indicate the presence of a large source of these ions which may allow them to enter into soil solution form.

4.3.4.3 Phosphate Mineral Solubility Diagrams

4.3.4.3.1 Calcium and Magnesium Phosphate Minerals

Calcium and magnesium ions precipitate with phosphate in supersaturated solutions (Abbona et al, 1986). The lower concentration of calcium and magnesium two months after the addition of MAP fertilizer compared to the control may possibly be related to the decrease in soil solution phosphate after the addition of MAP fertilizer (Tables 4.5 and 4.6). As discussed in 4.3.4.1, the precipitation of P with Ca or Mg cannot account for the total decrease in phosphate concentration. However, the precipitation of P minerals associated with calcium and magnesium is an important component of chemical reactions between soil and P fertilizer.

Solubility diagrams of P minerals depict the saturation index (SI) values of different P minerals in graphical form. As can be seen in Figures 4.5 to 4.8, calcium phosphate minerals are in equilibrium with phosphate levels in soil solution at all times after the addition of MAP fertilizer.

P minerals could not precipitate from solution within one hour of the addition of MAP fertilizer (Abbona et al, 1986). The solubility diagrams of P minerals depict SI values only and do not indicate P mineral precipitation. One hour after the addition of MAP fertilizer TCP and OCP are in equilibrium with soil solution (Figures 4.6 and 4.8), but probably have not precipitated out. However, the maintainance of equilibrium conditions between soil solution phosphate with P mineral solubilities for a two month period, may suggest that TCP and OCP are precipitating out of soil solution. The relationship of P minerals to the soil solution phosphate concentration of both samples indicate that similar processes are occurring in each sample.

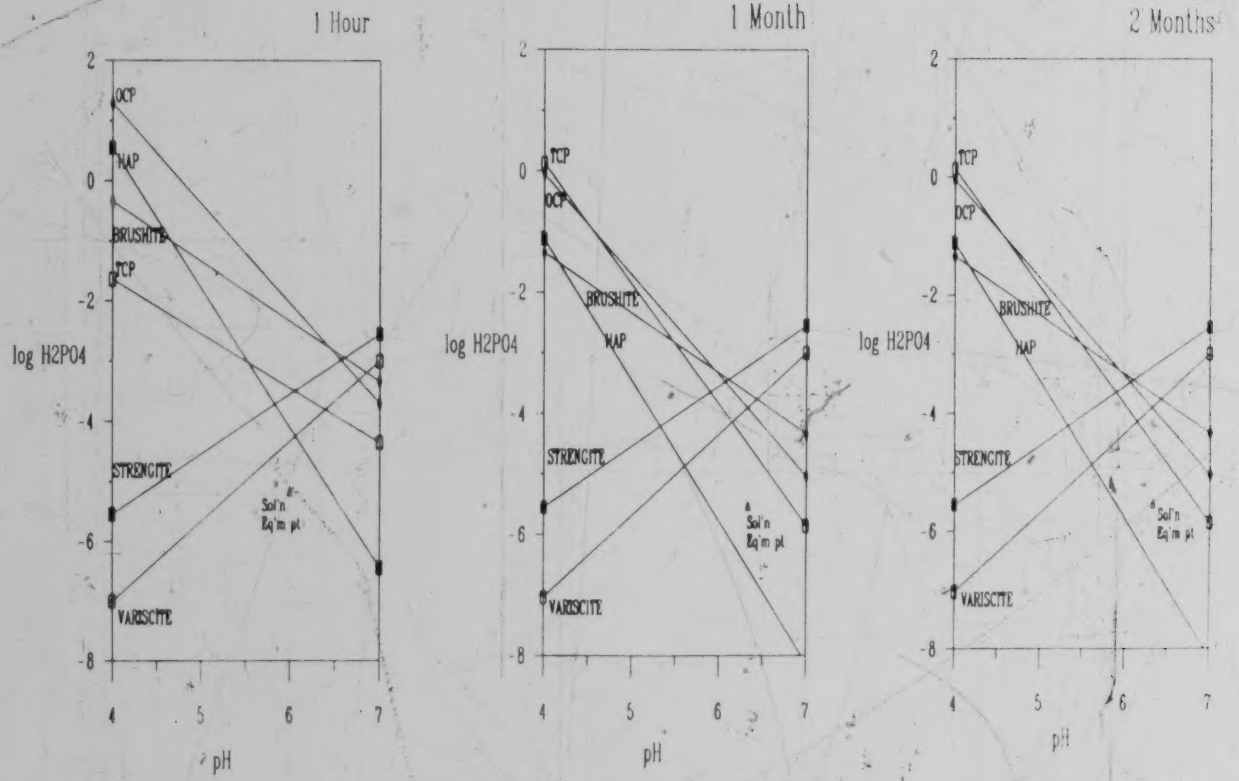


Figure 4.5. Phosphate mineral stability diagrams for Breton sample equilibrated at field capacity for two months.

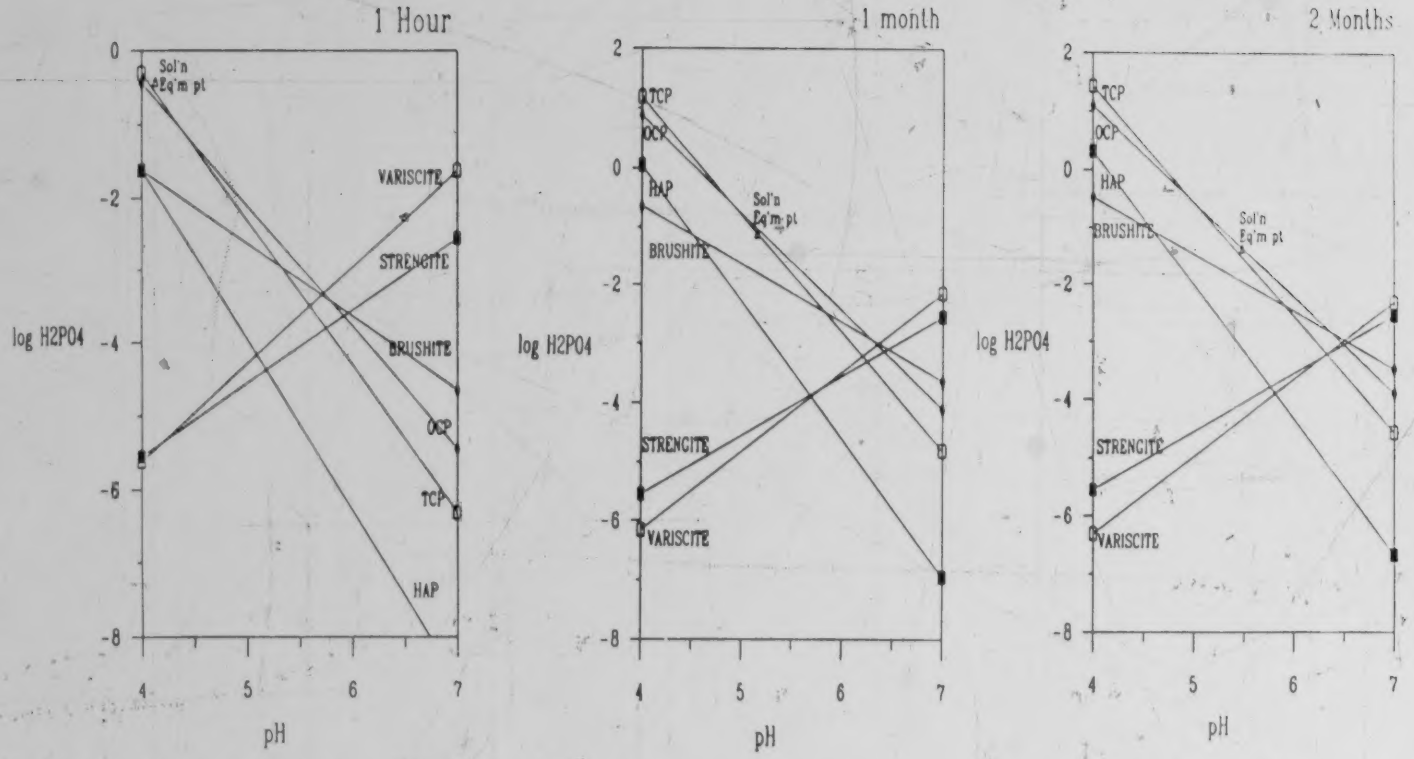


Figure 4.6. Phosphate mineral stability diagrams for Breton sample equilibrated at field capacity for two months after the addition of 5 mg P/g soil.

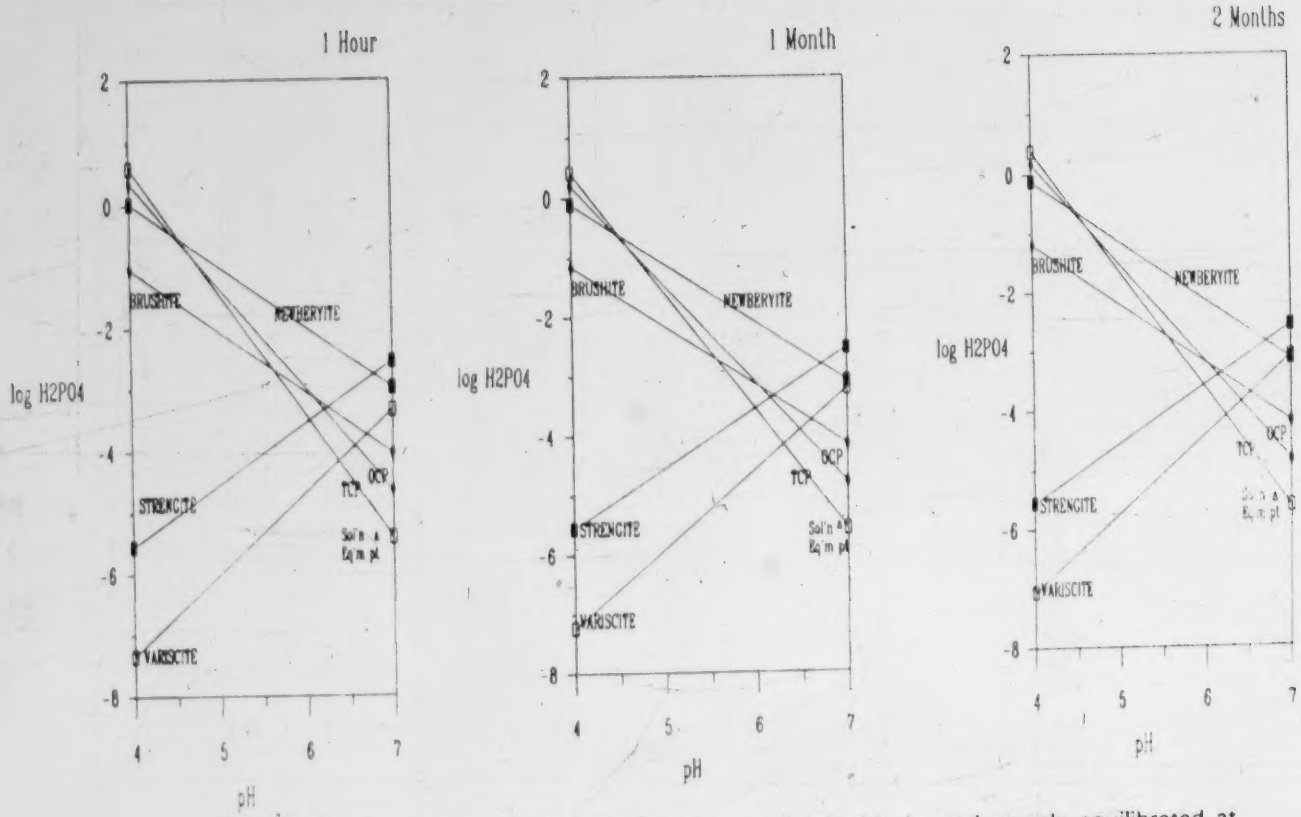


Figure 4.7. Phosphate mineral stability diagrams for Paddockwood sample equilibrated at field capacity for two months.

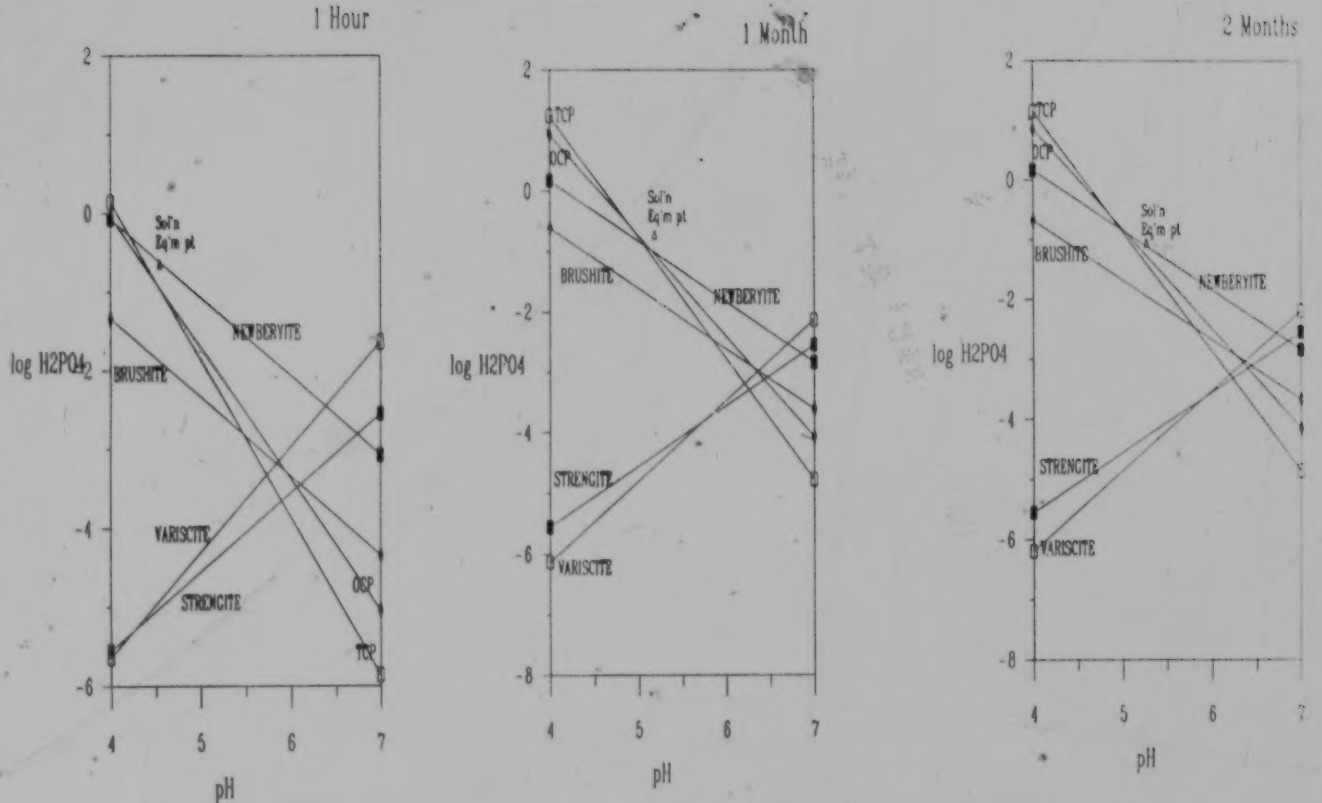


Figure 4.8. Phosphate mineral stability diagrams for Paddockwood sample equilibrated at field capacity for two months after the addition of 5 mg P/g soil.

4.3.4.3.2 Iron, Aluminium and Manganese Phosphate Minerals

The presence of iron and aluminium P minerals have been documented within the zone where P fertilizer reacts with soil (Sample et al, 1980). P minerals of iron, aluminum and manganese are undersaturated prior to, and are supersaturated after the addition of MAP fertilizer in both soils (Figures 4.5 to 4.8). The supersaturated condition of the solution with respect to P minerals of iron, aluminum and manganese after the addition of MAP fertilizer indicates high precipitation potential. Therefore, Fe, Al and Mn P minerals are definitely a potential sink for added P.

4.3.4.4 Fertilizer History and P Mineral Solubility Diagrams

The similarity in the dynamics of the ion concentrations in soil solution is remarkable considering the P fertilizer history of the two soil materials. The solubility diagrams of P minerals are also similar for the two soils. The annual addition of P fertilizer to the Paddockwood sample site for the 35 years prior to sampling does not seem to have affected the manner in which the soil reacts with added P.

Based on the dynamics of ion concentrationsin soil solution, added P may be reacting with the soil constituents in the same manner for both soils. Added P may simply be entering the soil P cycles of both soils. Residual added P in the Paddockwood sample must have been dispersed through cultivation so as to not allow the build up of zones of high P concentration in the soil.

4.3.4.5 Adsorption of Phosphorus

The precipitation of P minerals after the addition of MAP fertilizer could not possibly

account for the decrease in soil solution phosphate. The decrease in the amounts of calcium, magnesium, Al, Fe and Mn from soil solution after the high rate of addition of MAP fertilizer if tied up with phosphate could not account for the total decrease in the phosphate ion concentration over the same period. The only other option is that much of the phosphate has been removed from soil solution through its adsorption to soil minerals and organics.

4.3.5 Discussion of the Effects of Alfalfa Amendments on Soil Solution Values

The effects of the alfalfa amended to the soil samples during equilibration can mainly be attributed to alfalfa decomposition. The effects were mainly noticeable after one month of equilibration after which the soil solution values became similar to the non-alfalfa treatment (Table 4.6). The color of the soil solution may indicate the level of decomposition of alfalfa. After one month the pore water was very dark and contained high organic matter, whereas after two months of equilibration the pore water was the same yellow, clear color characteristic of the non-alfalfa treatment. The yellow color of the non-alfalfa treatment pore water is due to the solubilization of soil organic matter as a result of the low pH values (pH = 5.2). The dark color of the pore water after equilibration with alfalfa for one month is characteristic of organic matter dissolution through alkaline extraction. The pore water after equilibration with soil plus alfalfa for one month may represent the alkaline soluble fraction of organic matter. Therefore, the addition of MAP to soils high in organic matter may affect the alkaline aggregate stability.

Enriching the soil with an easily decomposible organic N compound with a low C:N (alfalfa meal) will always cause a rise in pH which is due to an accumulation of ammonia. The duration of such a pH increase will depend on the rate of alfalfa applied (Barnett and Dionne, 1980). The accumulated ammonia represents the quantity of substrate N in excess of microbial demand. The deamination of amino-acids with N mineralization releases ammonia which upon hydrolysis forms ammonium and increases the pH (Alexander, 1977).

The high pH of the pore water caused by excess ammonia must have undergone nitrification after extraction to account for the high nitrate values detected one month after the addition of MAP to the alfalfa treatment (Table 4.6). At high pH, nitrification occurs rapidly (Alexander, 1977).

Betremieux and Henin (1965) found that with the decomposition of lucerne, the pH of the solution became slightly alkaline, and the iron content in solution decreased. They also noted the evolution of soil organic matter.

The lower iron and manganese values in soil solution one month after the addition of MAP to the alfalfa treatment, corresponds to the period of highest decomposition of alfalfa. Betremieux and Henin (1965) noted that the decomposition of lucerne decreases the solubility of iron and manganese.

The removal of phosphate from soil solution after MAP addition to soil with an alfalfa amendment can be attributed to both adsorption and immobilization. Immobilization may occur during the initial decomposition of the carbon source where the C:P is high (300:1), especially when the carbon source is high in N. The CEC of organic materials doubles within 40 days of decomposition (Alexander, 1977); therefore $CaHPO_4$ complexes may be adsorbed to the organics at the low pH after two months of equilibration.

4.4 Characterization of Phosphorus in Fertilized Soil

4.4.1. Introduction

The mineral and organic components of soil are important factors that partially determine the fate of added P. Understanding the relationship of added P to mineral and organic soil components may compliment our previous discussion of soil solution dynamics after the addition of P fertilizer. The importance of understanding the relationship of added P to mineral and organic soil components is identified by the small amount of P in soil solution. For example the phosphate in soil solution amounted to 81% of Pt in the Breton

sample one hour after the addition of MAP fertilizer and decreased to 9% at two month. The phosphate in soil solution amounted to 47% of Pt

in the Paddockwood sample one hour after the addition of MAP fertilizer and decreased to 17% at two months. Therefore, to understand the fate of added P in the soil it is necessary to study the soil P distribution in addition to soil solution dynamics.

The Pt of each soil was analyzed by a sequential extraction procedure (O'Halloran et al, 1987). The sequential extraction procedure attempts to duplicate the effect a growing plant would have on the system by repeatedly depleating the soil solution of Pi. This technique isolates the various components of the soil P cycle according to their bioavailability (Roberts and Stewart, 1987).

The extractants involved in this fractionation procedure are: anion exchange resin (pH 8.2), 0.5M NaHCO3 (pH 8.2), 0.1M NaOH (pH 8.0), 1.0M HCl (pH 3.0) and H_2SO_4-H_2O_2 digestion. The sequential extraction procedure divides soil Pt into either five or seven fractions; two of the extractable fractions, 0.5M $NaHCO_3$ and 0.1M NaOH can be divided further into inorganic and organic components.

In the fractionation procedure each extractant is responsible for extracting different fractions of soil P (Roberts and Stewart, 1987). Resin- extractable P (Resin-P) is the most plant available form of Pi; it consists of the P minerals brushite and OCP, and also the Pi that is adsorbed to the surface of sesquioxides and carbonates. $NaHCO_3$ extractable P (Bicarb-P) is considered to consist of readily plant available Pi, slightly less available forms of the same components extracted by Resin-P and of easily mineralizable Po fraction. NaOH extractable P (NaOH-P) removes both the Pi component associated with amorphous and crystalline Al and Fe, and the Po component associated with stable organic forms. The HCl extractable P (HCl-P) consists of stable Ca-bound P, usually characterized by HAP. Finally,

acid digestion extactable P (Residual-P) consists of P associated with stable humus and humic acid and of insoluble Pi forms.

4.4.2. Changes in the Fractions of Phosphorous After the Addition of MAP Fertilizer and Subsequent Equilibration

4.4.2.1. Introduction

The sequential extraction technique was conducted on the equilibration samples that soil pore water was extracted from. After complete characterization of soil P fractions, comparison with pore water data may increase the understanding of soil-fertilizer reactions.

The Resin-P fraction generally decreased with time after MAP fertilizer was applied to the soil samples in the equilibration study. The decrease in Resin-P was complimented by increases in other less available P fractions in both Breton and Paddockwood samples. This decrease in Resin-P with time after the addition of MAP fertilizer may be related to the decrease in P concentration in soil solution. As the phosphate concentration in soil solution decreased, there was a corresponding decrease in the amount soil solution phosphate in Resin-P. Also, decreases in soil solution phosphate were generally greater than decreases in Resin-P. Therefore, phosphate that was leaving soil solution was becoming transformed to other soil P fractions in addition to solid forms of Resin-P.

4.4.2.2. Changes in the P Fractions of Breton Soil After the Addition of MAP Fertilizer

The soil P fractions were monitered one hour, one month and two months after the

addition of MAP fertilizer to the Breton samples. The continual decrease of Resin-P over the two month time period was matched by simutaneous increases of Bicarb-Pi, NaOH-Pi,NaOH-Po and HCl-P (Table 4.8). The highest increases were in the Bicarb-Pi and NaOH-Po fractions. The P associated with the Bicarb-Pi fraction remains readily available, while the P associated with NaOH-Po is more stable (Roberts and Stewart, 1987). A major portion of added P also occurs as relatively insoluble calcium phosphate minerals associated with HCl-P.

The amount of soil solution P in the Resin-P fraction after the addition of MAP fertilizer to the Breton sample decreases with time. For example, one hour after the addition of MAP fertilizer, soil solution phosphate virtually equals Resin-P (Table 4.9). However, one month later soil solution phophate accounts for 32% of Resin-P; and at two months this value is 19%. Over the two month duration of the equilibration experiment, the amount of soil solution phosphate in the Breton sample decreased by about 3200 μg P g^{-1} (calculated from Table 4.5) soil while the amount of Resin-P decreased by about 1300 μg P g^{-1} soil (Table 4.9).

4.4.2.3. Changes in the P Fractions of Breton Soil With Alfalfa Amendment After the Addition of MAP Fertilizer

When alfalfa was added to the Breton sample in addition to MAP fertilizer, the P transformations between soil P fractions during equilibration were similar to treatments without alfalfa addition. However, the amount of P undergoing transformations was much lower with the alfalfa amendment than without it. More P was retained in Resin-P fraction, and lower levels of NaOH-P and HCl-P were attained.

When alfalfa and MAP fertilizer were added to the Breton sample, the amount of soil solution phosphate in Resin-P strongly decreased with time (Table 4.9). For example one

TABLE 4.8. Difference means of soil P fractions for equilibration study soils.

	Concentration of P in equilibating soil (mg P/g soil)								
	5.2			16			5.2 + Alfalfa		
	Equilibrating Time (days)								
P Fraction	1hr	30	60	1hr	30	60	1hr	30	60
	μg P/g soil								
				BRETON					
RESIN-P	3333	2107	2036	7570	10181	8789	2743	2221	2281
NaHCO3-Pi	335	740	919	1023	1826	1984	586	865	893
NaHCO3-Po	0	0	0	118	820	531	0	21	0
NaOH-Pi	65	234	224	908	6440	3729	104	93	150
NaOH-Po	125	688	730	180	0	101	266	490	500
HCl-P	160	259	467	235	1549	999	125	253	325
RESIDUAL	0	7	0	0	58	10	46	16	0
Total P	4368	4337	4223	10034	20874	16143	3870	3959	4149
LSD1(0.05)	608								
LSD2(0.05)	173								
				PADDOCKWOOD					
RESIN-P	2943	2630	2907						
NaHCO3-Pi	292	634	479						
NaHCO3-Po	204	1	0						
NaOH-Pi	147	532	411						
NaOH-Po	26	108	39						
HCl-P	58	78	91						
RESIDUAL	0	0	0						
Total P	4740	3984	4616						
LSD3(0.05)	108								
LSD4(0.05)	264								

LSD (0.05) = least significant difference at the 0.05 probability level between the Breton sample treatment means (LSD1), between the Breton sample treatment means excluding the high rate (16mg P/g soil) of P addition (LSD2), between the Paddockwood treatment means (LSD3), and between the Paddockwood and Breton treatment means (LSD4)

TABLE 4.9 Soil solution phosphate expressed as a percentage of the Resin-P fraction after the addition of the low rate of MAP fertilizer

Sample	1hr	30 days	60 days
	%		
Breton	90	32	19
Breton with alfalfa	60	6	5
Paddockwood	76	66	28

hour after the addition of MAP fertilizer, soil solution phosphate amounts to 60% of Resin-P; after one month this value is 6% and after two months this value is 5%. Over the two month duration of the equilibration experiment, the amount of soil solution phosphate in the Breton sample with alfalfa amendment decreased by about 1674 μg P g^{-1} soil while the amount of Resin-P decreased by about 522 μg P g^{-1} soil (Table 4.9).

4.4.2.4 Changes in P Fractions of Paddockwood Soil After the Addition of MAP Fertilizer

During the equilibration experiment, the transformations between P fractions are also similar for the Paddockwood sample and the Breton sample. Although a few differences do exist. For example, there is no measured decrease in Resin-P, however the soil solution phosphate concentration decreases with time.

The amount of soil solution phosphate in Resin-P after the addition of MAP fertilizer to the Paddockwood sample also decreases with time (Table 4.9). For example one hour after the addition of MAP fertilizer, soil solution phosphate amounts to 76% of Resin-P; after one month this value is 66% and after two months this value is 28%. Over the two month duration of the equilibration experiment, the amount of soil solution phosphate in the Paddockwood sample decreased by about 1426 μg P g^{-1} soil, about one half of the Breton value (Table 4.9). A decrease of Resin-P over this period is not detected.

4.4.3. Discussion of the Changes in P Fractions After the Addition of MAP Fertilizer

4.4.3.1 Introduction

Transformations of P between fractions after the addition of MAP fertiiizer follow

similar pathways between soils. P transformations were larger for the Breton sample than for the Paddockwood sample. The P transformations for the Breton sample with the alfalfa amendment were of a similar scale to the Paddockwood sample.

P added to the soil generally moves from plant available forms (Resin-P) to less readily available forms. P moves into most forms directly from soil solution. Soil solution phosphate undergoes both precipitation and adsorption reactions and remains in the Resin-P fraction. However, the majority of the decrease in Resin-P probably occurs as direct movement of soil solution P to other P fractions through precipitation, adsorption, and chemi-sorption.

Most of the P transformations within two months after the addition of MAP fertilizer is from Resin-P to Bicarb-Pi. 50% of added P in the Breton sample and 70% of added P in the Paddockwood sample remains in Resin-P and Bicarb-Pi fractions. Wagar et al (1986) found that after both five to eight years of addition of P fertilizer to two Saskatchewan soils, 50% of fertilizer P remaining in the soil existed in the Resin-P and Bicarb-Pi fractions.

4.4.3.2 Discussion of Changes in P Fractions After the Addition of MAP Fertilizer to the Breton Sample

The movement of P out of soil solution after the addition of MAP fertilizer to the Breton sample indicates a decrease in available P forms. The P can move from soil solution to all soil P fractions. Some will remain as Resin-P and the rest will move directly from soil solution to the less available fractions.

The majority of added P in the Breton sample remains in the readily available Resin-P fraction for at least two months. Resin-P contains soil solution P, soluble P mineral

precipitates and adsorbed Pi. Therefore, most of the added P remains available for plant uptake for the two months.

Added P in the Breton samples also moves from soil solution to Bicarb-P through precipitation and adsorption reactions. Bicarb-P contains slightly less available forms of P than Resin-P. The Bicarb-P in the Breton soil will then serve as a labile P source to Resin-P.

The increase of NaOH-Po in the Breton samples after the addition of MAP fertilizer is the result of complex reactions. The Breton sample has low carbon content, so the generation of 600 μg P g^{-1} soil is unlikely. Therefore, the increase in NaOH-Po is probably not actual Po. The NaOH-Po increase is probably the result of selective adsorption of P to stable organic compounds associated with iron and manganese (Appelt et al, 1975).

The increase of HCl-P in the Breton samples after the addition of MAP fertilizer may result from P mineral precipitation with a subsequent increase in pH. Calcium phosphate minerals are more soluble at the pH levels found in soil solution just after the addition of MAP fertilizer. The increase in soil solution pH with time decreases the solubility of the precipitated calcium phosphate minerals. Therefore with the increase in pH of soil solution, calcium phosphate minerals may move from Resin-P to HCl-P because of the change in solubility.

4.4.3.3 Discussion of Changes in P Fractions After the Addition of MAP Fertilizer and Alfalfa Amemdment to the Breton Sample

The transformations between the P fractions of the Breton sample with the alfalfa amendment are occurring for similar reasons as in the Breton sample without the alfalfa amendment. Even the increase in NaOH-Po is similar to that of the non-alfalfa treatment and is therefore likely the result of adsorption of P to Al, Mn and Fe organics.

4.4.3.4 Discussion of Changes in P Fractions After the Addition of MAP Fertilizer to the Paddockwood Sample

After the addition of MAP fertilizer to the Paddockwood samples, the movement of P out of soil solution is not associated with a decrease is Resin-P. The low decrease in Resin-P may result from P mineral precipitation and from phosphate adsorption to sesquioxidic nodules that are part of this fraction. The P source for increases in Bicarb-Pi and NaOH-Pi may be undetected decreases in Resin-P.

The prior addition of P fertilizer to the Paddockwood sample has probably caused an adjustment in the steady state conditions of the soil P cycle. Therefore, higher levels of P would be associated with all components of this soil P cycle (McKenzie, 1989). The high P content of each component of the soil P cycle may reduce the movement of added P away from the most readily plant available form. Therefore, Paddockwood sample Resin-P values may remain nearly constant with time.

4.4.4. Distribution of Added Phosphorus After Barley Growth

4.4.4.1 Introduction

Analysis of P distribution within fractions after crop growth may lead to an understanding of the role these different P fractions have in uptake of P. After barely was grown in greenhouse soil samples for three months, added P was observed by three methods. The plant material was analysed for P uptake, soil P fractions were analyzed and soil thin sections were analyzed for direct observation of P distribution.

P abundance decreased with distance from the fertilizer granule until, at 2 - 3 cm, it

was similar to the control treatment. The P increases near the fertilizer granule were distributed among the P fractions at similar ratios to the equilibrium experiment. The similarity between the greenhouse sample P fractions and the equilibration sample P fractions indicate the same P transformation processes were occuring in the soils of each experiment.

The amount of P involved in the P fractions of the greenhouse samples is lower than the equilibration samples, so comparisons will be dealt with on a relative scale. Distribution within fractions of the greenhouse samples is generally similar to the equilibration samples. Resin-P fractions account for relatively the same amounts of P as the equilibrated treatments in both Breton and Paddockwood samples. The Bicarb-P in greenhouse samples is generally lower, possibly reflecting P uptake by plants.

Large amounts of NaOH-P were found in Breton and Paddockwood samples under both experimental conditions. NaOH-P accounted for approximately 20% of Paddockwood Pt and 33% of Breton Pt in the greenhouse soil samples. Wagar et al (1986) measured relatively small amounts of fertilizer P recoverable by NaOH in Waskada soils whereas NaOH-P accounted for 36% of fertilizer P remaining in a Sutherland soil after five years. Therefore, values obtained in this experiment are similar to those values attained after long term fertilization.

The similarities of P distribution in soil after long term P fertilizer addition and our short term experiment may mean P transformation pathways between fractions are similar for both time periods. Therefore, the soil P cycle must be similar for both soils, with different steady state conditions existing for each sample.

4.4.4.2 Distribution of Added P After Barley Growth on Breton Samples

After three months of barley growth, approximately 50% of the P remaining in Breton samples is retained in readily available Resin-P and Bicarb-P forms (Table 4.10). This is similar to values found in the equilibrated samples and to values found by Wagar et al (1986). Therefore, except for the Po returned to the soil in crop residue forms, the P cycle may reach steady state conditions by the end of the growing season.

4.4.4.3 Distribution of Added P After Barley Growth on Paddockwood Samples

After three months of barley growth 75% of the P remaining in Paddockwood samples is retained in readily available Resin-P and Bicarb-P forms. This may reflect the low decrease in Resin-P in the Paddockwood samples of the equilibration study.

4.4.5 Discussion of the Changes in P Fractions After Barley Growth

The non-replication of P fractionation analysis of the greenhouse samples does not allow for statistical analysis. Therefore, definite statements about P transformation processes cannot be made. However, general observations depict similar effects happening near the fertilizer pellets in the greenhouse samples as were occurring in the equilibration samples.

The only noticeable effect that the growth of barley may have had on the P distribution among soil fractions is a decrease in labile P (Bicarb-P). This may indicate that as plants take up phosphate, it may move from Bicarb-P form to Resin-P form.

TABLE 4.10. Greenhouse soil P fractions after P addition and 3 months of barley growth.

	Size of MAP fertilizer pellet(g)					
	0.01			0.10		
	Distance of soil sample from fertilizer pellet (cm)					
P Fraction	0-1	1-2	2-3	0-1	1-2	2-3
	—μg P/g soil—					
			BRETON			
RESIN-P	58	3	1	493	333	48
NaHCO3-P	52	3	0	147	138	0
NaOH-P	114	92	0	391	251	0
HCl-P	0	68	20	146	59	50
RESIDUAL	26	23	0	5	15	0
Total-P	250	189	21	1182	796	98
			PADDOCKWOOD			
RESIN-P	354	345	0	649	450	41
NaHCO3-P	92	92	0	220	102	15
NaOH-P	98	120	0	236	85	0
HCl-P	84	84	8	34	44	3
RESIDUAL	9	0	0	37	3	0
Total-P	637	641	8	1176	684	59

4.4.6. Forms and Distribution of Added Phosphorus as Seen in Soil Thin Sections

Thin sections of the undisturbed soil near the fertilizer granule within the greenhouse experiment soil samples give an excellent depiction of the soil environment including products of reactions between the soil and fertilizer P. Both P adsorption to soil minerals and P precipitation products are clearly shown. The locations and distribution of areas of high P concentration within the soil fabric are also clearly evident. The evidence is particularly good for the Paddockwood samples. Although thin section evidence has not been found, similar reactions are most certainly occurring in the Breton samples, based on similarities in P mineral solubility diagrams and on P fractionation values (Figures 4.5 and 4.6 and Tables 4.8 and 4.10),

P levels in the soil thin sections were measured semi-quantitatively by EDX. Fairly high quantities of P must be present because of low detection limits of EDX. Much of the distribution of added P that is present in low concentrations in the soil, could not be detected.

The concentration of adsorbed P in % per g soil would normally be so low that it would not be detected by the EDX. However, the P on the surface of an iron/manganese nodule in Plate 4.2 has concentration high enough to be detected.

P mineral crystals have been found in soil thin sections within a 1cm radius of 0.10g MAP granules and within a 1.5cm radius of 0.50g MAP granules. The P mineral crystals are exclusively associated with calcium ions. These calcium phosphate minerals occur in voids adjacent to soil minerals (Plates 4.3 to 4.5).

Plate 4.2. Depictions of nodules in Paddockwood sample thin sections near the application site of MAP fertilizer: (a) micrograph in plane light (frame length = 3.5mm); (b) SEM scan of the same area

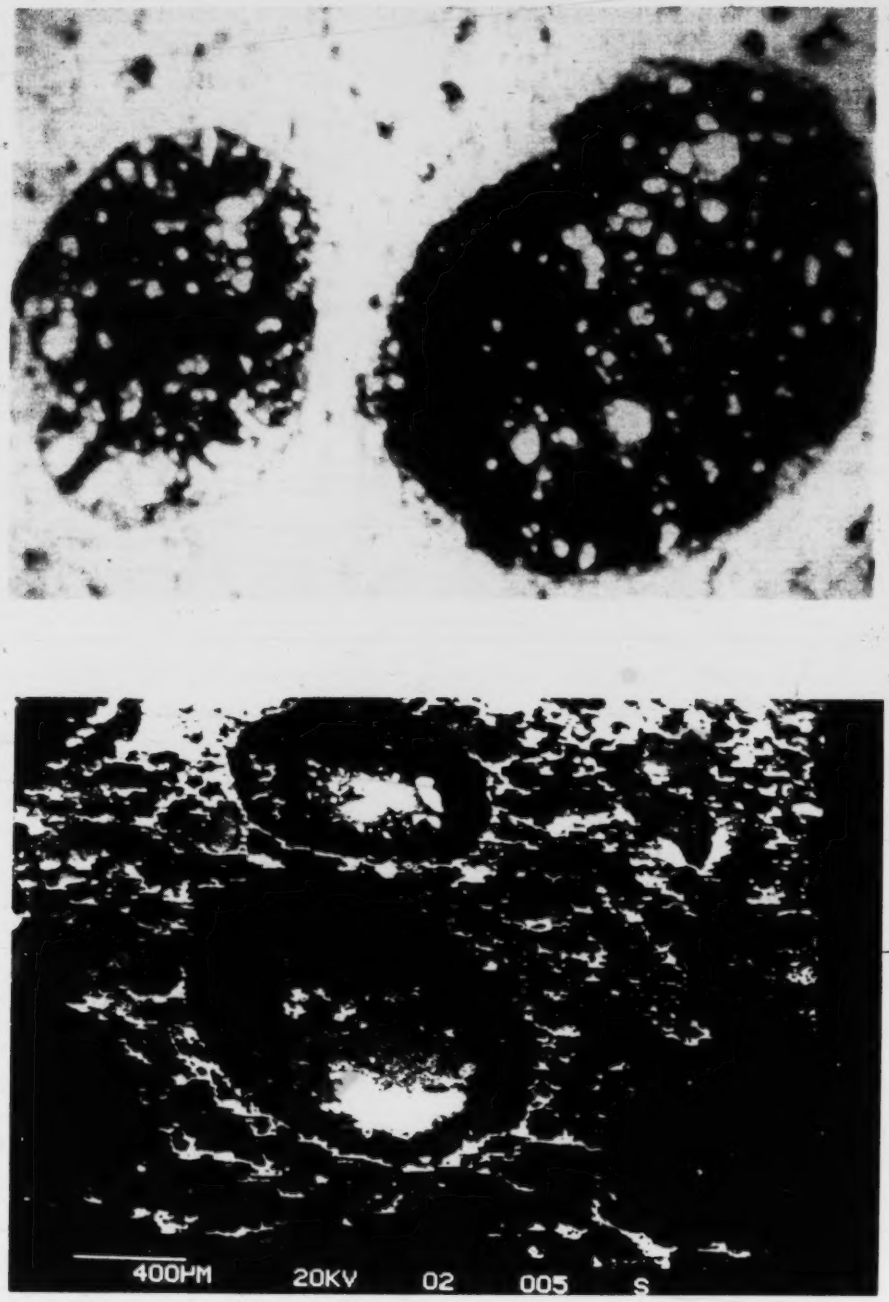
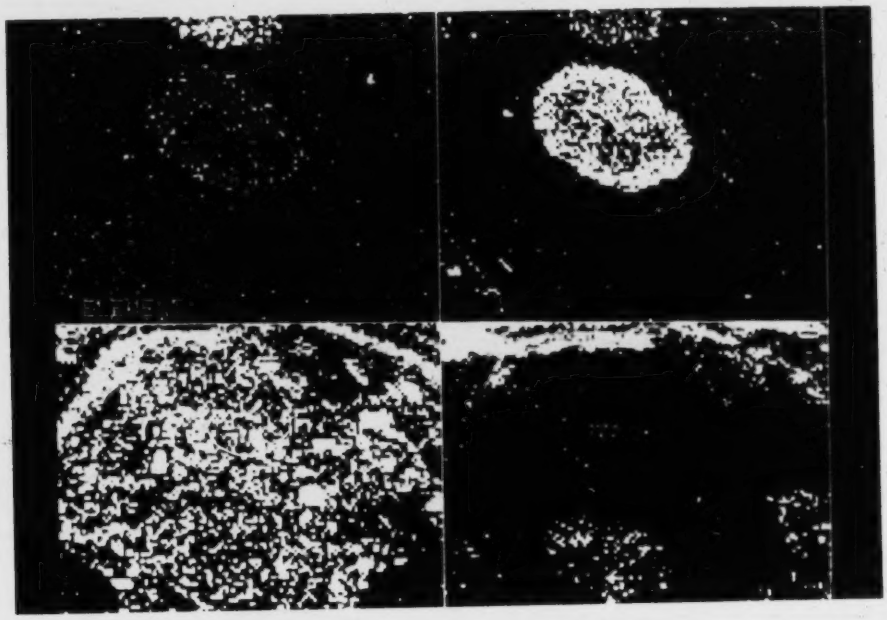


Plate 4.2. continued: (c) EDX map showing the nodules to be of iron and manganese oxides; (d) showing P association with the nodules and not with calcium.



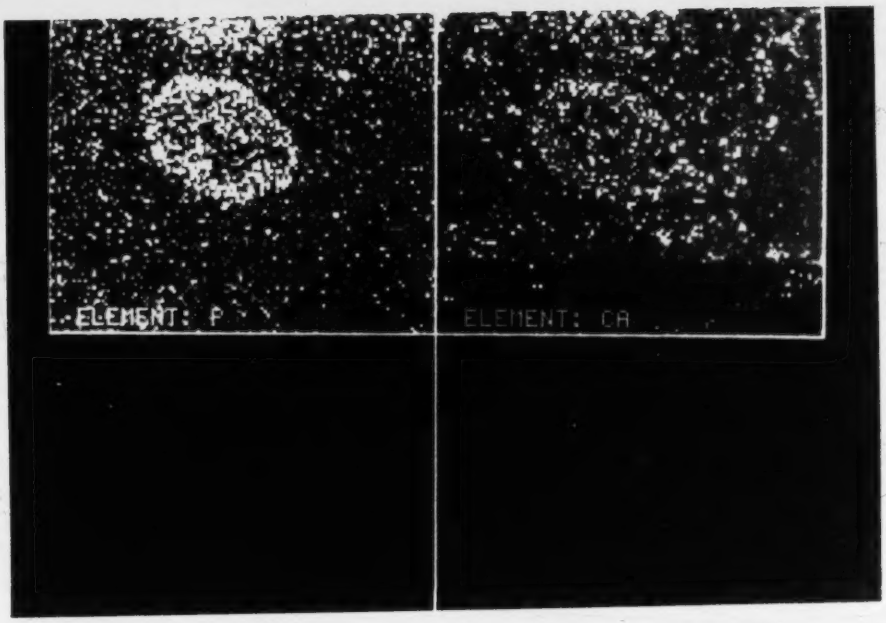
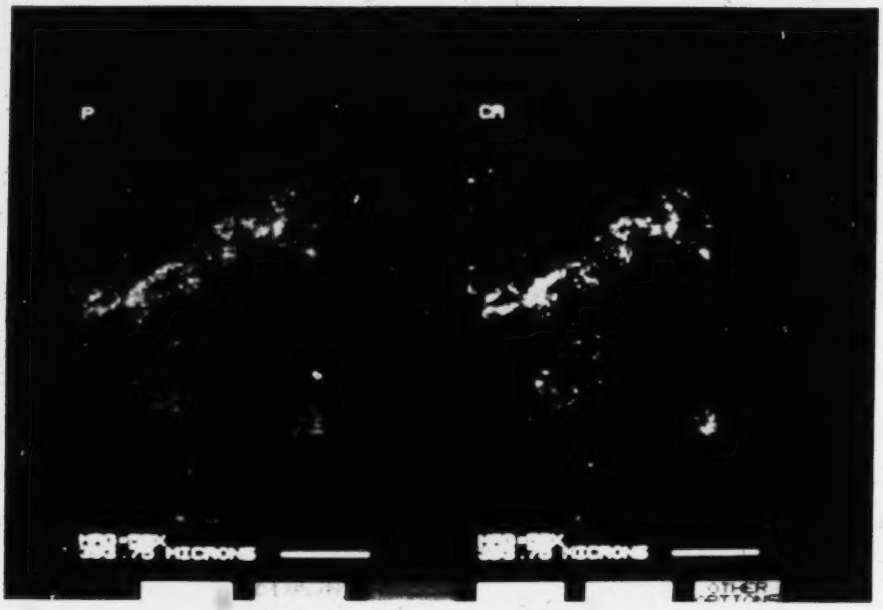


Plate 4.3. Depictions of nodules in Paddockwood sample thin sections near the application site of MAP fertilizer: (a) The association of calcium with added phosphorus; (b) calcium phosphate accumulations in voids of the soil matrix;



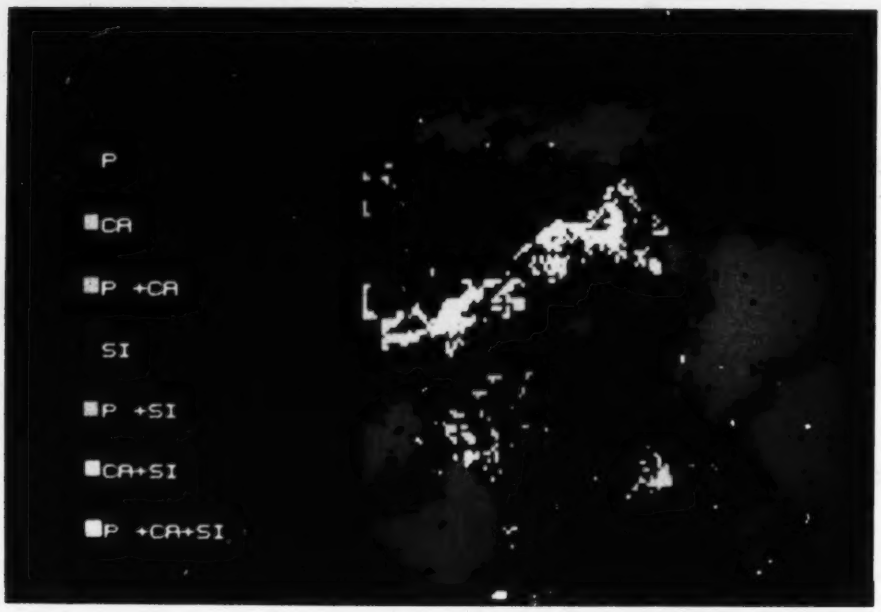


Plate 4.3. continued: (c) calcium phosphate accumulations in voids left by the fertilizer

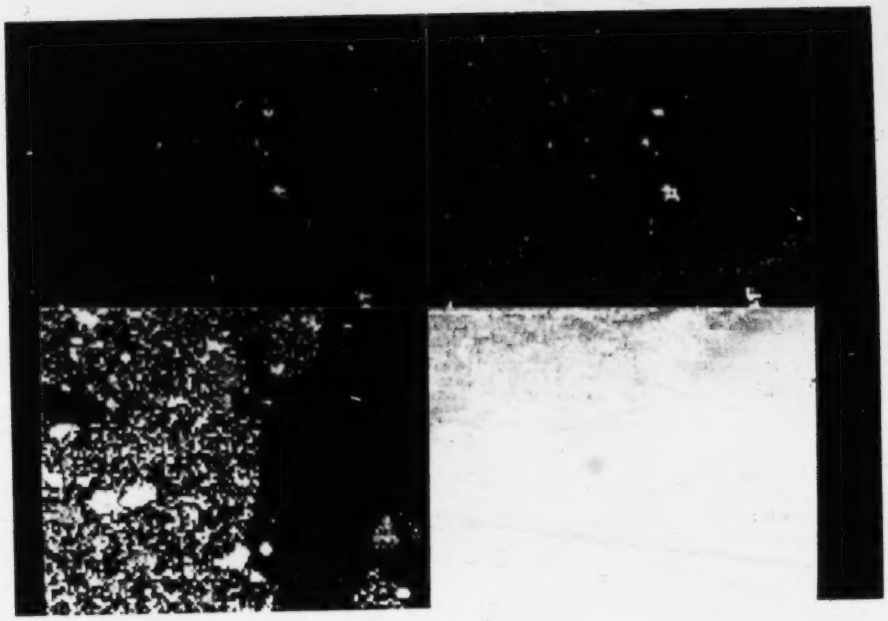


Plate 4.4. Micrographs showing calcium phosphate minerals adjacent to soil fabric in voids left by the granule of MAP fertilizer: (a) plane light (frame length = 3.5mm); (b) with filters under cross polarized light (frame length = 3.5mm).

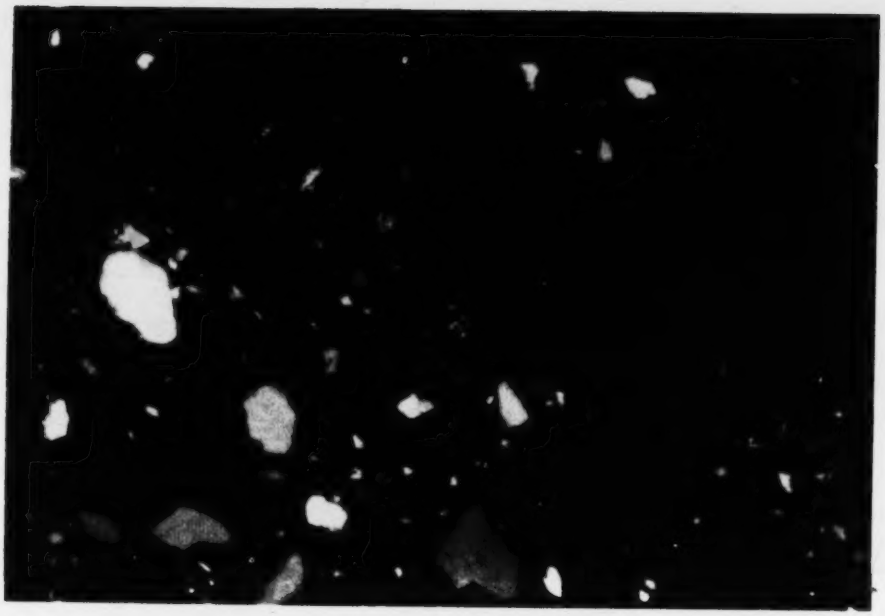
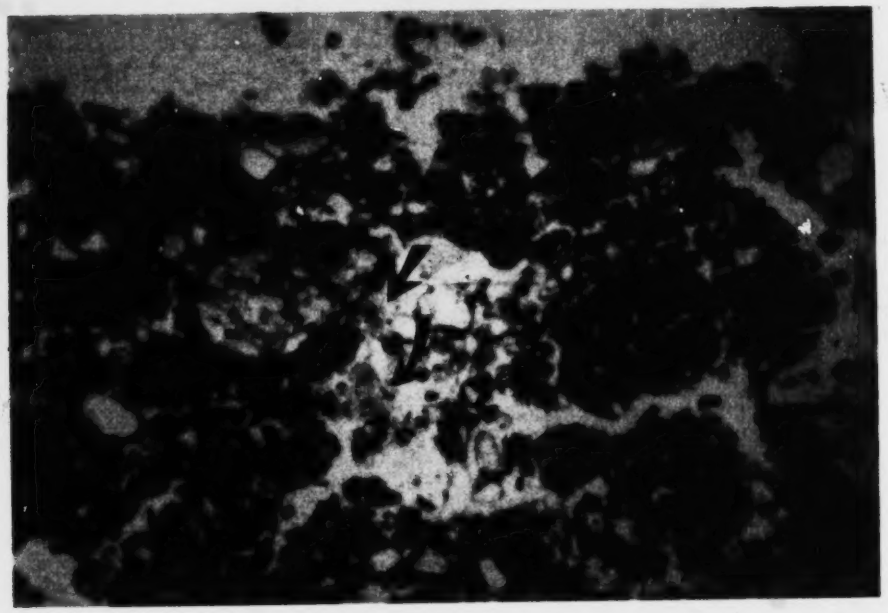


Plate 4.5. Micrographs showing calcium phosphate minerals adjacent to soil minerals in voids: (a) in plane light showing distribution in the soil matrix (frame length = 7.0mm); (b) with filters under cross polarized light (frame length = 7.0mm);



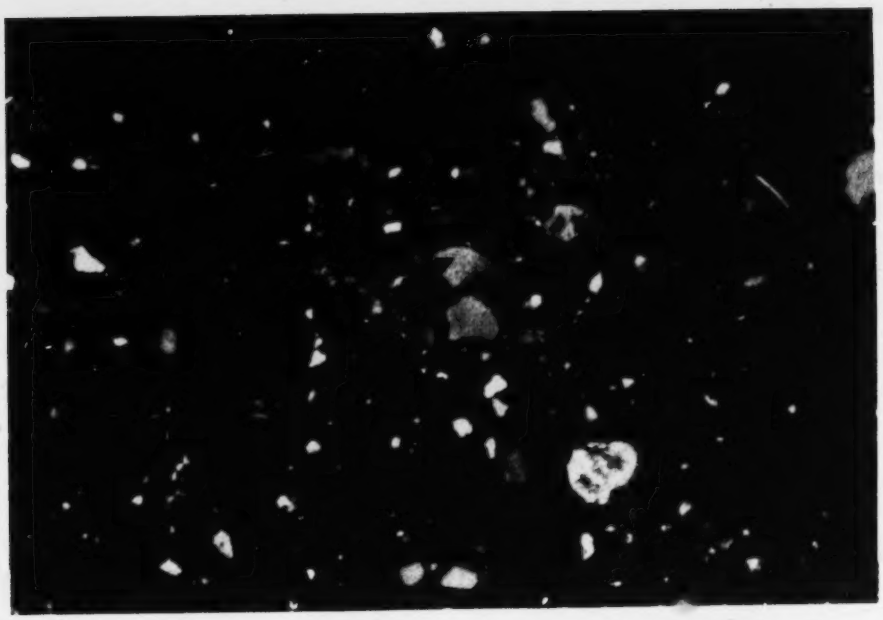
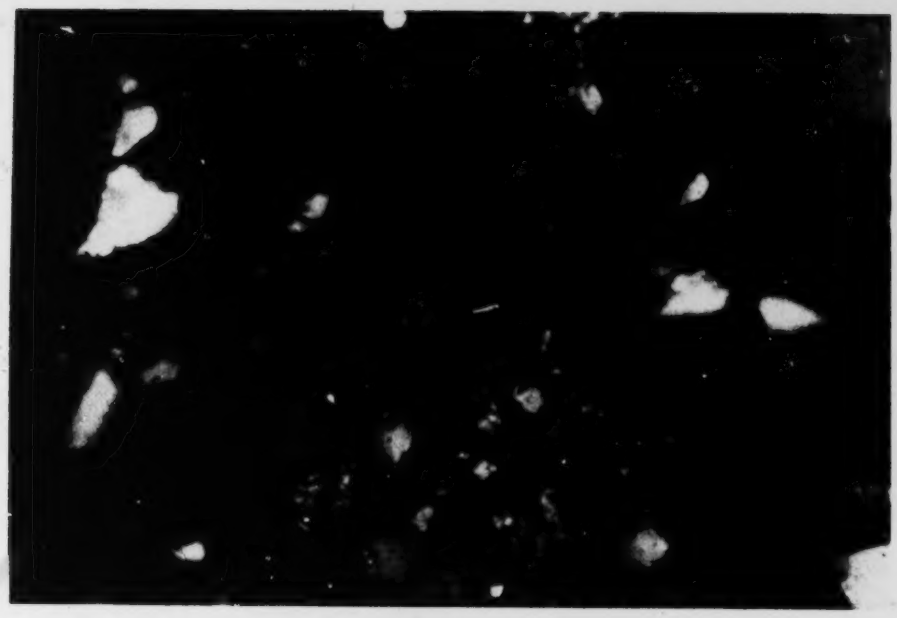


Plate 4.5. continued: (c) in plane light (); (d) with filters under cross polarized light (frame length = 0.5mm).



The most common calcium phosphate minerals appear to be OCP and Brushite. OCP crystallizes as thin blades arranged in a radial pattern (Plate 4.4) (Lehr et al, 1967). Brushite is present as a larger crystal with a brownish color in plain light with crystal habits that resemble gypsum (Plate 4.5). These OCP and Brushite minerals are located in voids left by the MAP fertilizer granule and in packing voids further away from the granule.

4.4.7. Discussion of Thin Section Evidence

The thin section evidence clearly showed detectable P accumulations to be more abundant in the Paddockwood soil samples than in the Breton soil samples. As discussed earlier, the Paddockwood site has had a previous history of P fertilizer addition whereas the Breton site has not. So the more abundant P accumulations of the Paddockwood sample thin sections may be a result of either the previous fertilizer history of the soil or the soil properties themselves.

Thin sections from the Paddockwood control sample, that was not treated with MAP fertilizer in the greenhouse, did not provide any evidence of P accumulation. So the P accumulations in thin sections of Paddockwood samples after barley growth and fertilizer addition could be attributed to the MAP fertilizer addition. All the P crystals found were located near the fertilizer granule sites (Plate 4.1). P accumulation onto sesquioxidic nodules was also limited to the nodules located near the fertilizer granules (Plate 4.2). The large amount of P fertilizer that has accumulated in the soil over the years has probably generated nuclei that increase the rate of P mineral precipitation, thus enabling faster crystal formation in the Paddockwood sample.

The correlation between the distribution of fractions in the greenhouse and equilibration samples is very good. A good relationship also exists between the soil thin

sections, taken from the greenhouse samples, and the P mineral solubility diagrams derived from equilibration soil data.

Although OCP, TCP, Brushite and Newberyite all seem to be in equilibrium with Paddockwood soil solution (Figure 4.6), OCP and Brushite are the dominant P minerals present. The presence of Brushite and OCP minerals verifies the validity of the P mineral solubility diagrams. These Brushite and OCP minerals must be controlling the soil solution phosphate levels in soil. If they control soil solution phosphorus concentrations, they definitely contribute to the Resin-P fraction.

As the soil pH increases the Brushite and OCP minerals will become less soluble (Figure 4.6 and 4.8). The Resin-P fraction will decrease as the Brushite and OCP minerals become more stable and revert to the HCl-P fraction.

The P accumulated on the surface of the sesquioxidic nodule in Plate 4.2 has moved 1.5 to 2 cm from a 0.50g MAP pellet. The soil that the added P moves through is a packed greenhouse soil with fabric as described in Table 4.11. Therefore, a large amount of added P is moving through the soil. These quantities and distances are similar to those found by Bell and Black (1970b).

The P accumulated on the surface of the sesquioxidic nodules may be either attached through anion adsorption or precipitated as surface coats of Fe or Mn phosphate minerals. The potential for the precipitation of Fe and Mn P minerals is evident from the soil solution data. Iron phosphate minerals are more stable than iron oxides in soil. The potential for phosphate adsorption to the sesquioxidic nodule is also high because the low pH will give rise to high anion exchange capacity because of the pH dependent charge of the oxides. Regardless, the relationship between P and the sesquioxidic nodules increase the NaOH-P fraction.

TABLE 4.11. Micromorphological description of potted greenhouse soil samples at depths from 1 to 6 cm.

Paddockwood

Sequence: Granic

Type: Matri-granoidic porphyric//porphyric

Description: Dominant fabric type is matri-granoidic porphyric with common matri-porphyric fabric. Size of granoidic units varies from 0.5mm to 2.0mm with an average of 1.0mm diameter. Granoidic units are composed of soil plasma and frequent quartz and feldspar grains. Few zones of iunctic porphyric fabric are also present. Voids are comprised of craze planes (15%) and fine to medium, irregular, ortho vughs (10%) and comprise of 25%/unit volume of soil. Packing voids are also present in a few areas.

Pedological feature: (i) Few, discrete, spherical, sesquioxidic nodules with sharp boundaries and undifferentiated fabric. They range in size from 1mm to 3mm in diameter. (ii) Very few spherulitic, phosphitic crystals within voids, adjacent to soil matrix.

Plasma fabric: Dominant fabric type is silasepic. Nodules also have silasepic fabric.

Breton

Sequence: Granic

Type: Matri-granoidic porphyric

Description: Dominant fabric type is matri-granoidic porphyric with frequent matri-granoidic and iunctic-porphyric fabric. Size of granoidic units vary from 0.4mm to 1.5mm with average of 0.8mm diameter. The granoidic units are composed of soil plasma with frequent quartz and feldspar grains. Zones of fragmoidic porphyric fabric are also present. Voids comprise 30% of soil volume and 30 to 50% above the seed row. Fine to medium irregular ortho vughs are frequent with a few interpedal meso joint planes.

Pedological feature: (i) Common discrete spherical sesquioxidic (8%) and manganiferous (5%) nodules with sharp boundary and lamellar fabric. They range in size from 0.2mm to 1.0mm with an average of 0.8mm diameter. (ii) Very few discrete, rectangular, single ortho-aggrotubule (2.5mm).

Plasma fabric: Dominant fabric type is silasepic. Nodules are mosepic. Aggrotubules are silasepic.

4.5. Granule Size and Band Placement of P Fertilizer

The granule size and band placement of MAP fertilizer were both varied in the greenhouse study. These two factors were studied to develop and understanding of the utilization efficiency of P fertilizer. Also, granule size and band placement are the two factors that could most easily be adjusted to increase the efficiency of P fertilizer on a practical level.

4.5.1 Effects of the Granule Size of MAP Fertilizer on Phosphorus Uptake and Barley Growth

Different treatments were tested to determine how P fixation varies with fertilizer granule size. In the Breton samples the distribution between soil P fraction of each pellet size treatment varied from the P distribution within the equilibration treatment. For example, the 0.10g pellet treatment had relatively lower Bicarb-P and the 0.01g pellet treatment had relatively lower Resin-P (Table 4.10).

In the Paddockwood samples, the distribution between soil P fractions for both granule size treatments exhibit trends similar to that for the equilibration soil treatments. The majority of the added P remained in the Resin-P form (Table 4.10). Significant increases were determined for the Bicarb-P and NaOH-P fractions. In addition, there was no difference in the HCl-P and Residual-P fractions.

The efficiency of uptake by barley from each granule size of MAP fertilizer was measured. The solution form of MAP had higher P uptake from the Breton soil sample after one month than other granule size treatments (Table 4.12). This treatment probably had the greatest distribution of P and was therefore the most available for the early growth of

TABLE 4.12. Uptake of added ^{32}P by barley from Breton and Paddockwood soils for pellet size, pellet placement and organic amendment treatments.

Form of fertilizer	Harvest time periods (days)					
	BRETON			PADDOCKWOOD		
MAP[&]	30	60	90	30	60	90
	mg ^{32}P					
Solution P[#s]	2.8	5.9	T2.3	2.1	5.4	12.3
0.01g[s]	2.5	5.8	11.5	2.0	6.1	11.9
0.10g[s]	2.5	6.1	11.9	2.3	6.8	12.6
0.50g[s]	1.5	6.8	12.3	1.7	6.6	10.9
Straw[s]	2.2	6.3	12.1	2.0	7.2	13.3
Peat[s]	2.3	7.1	14.2	2.7	6.8	13 8
0.01g[d]	0.7	4.9	8.0			
0.10g[d]	0.9	5.5	9.2			
0.50g[d]	0.2	3.9	8.0			

& Fertilizer MAP was added at a rate of 20 kg/ ha, and K2SO4 and NH4NO3 were added at rates of 20 and 50 kg/ha, respectively.
# Fertilizer was dissolved water and added as a band.
d Fertilizer was banded 10 cm below the seed row.
s Fertilizer was banded 2cm below and 2cm beside seed row.

Significance levels for various treatment contrasts from analysis of variance of uptake of ^{32}P by barley from Breton and Paddockwood greenhouse soil samples.

Orthogonal Contrasts	Harvest time periods (days)					
	BRETON			PADDOCKWOOD		
	30	60	90	30	60	90
soln vs granular	0.005	ns	ns	ns	0 02	ns
lo,hi vs mid	0.05	ns	ns	0.005	ns	0 0001
0.01g vs 0.50g	0.001	ns	ns	ns	ns	ns
0.1g vs 0.1g + org	ns	ns	0.005	ns	ns	ns
Peat vs Strw	ns	ns	0.02	0.005	ns	ns
Nonorthogonal Contrasts						
0.01g[s] vs 0.10g[s]	ns	ns	ns	ns	ns	ns
0.50g[s] vs 0.10g[s]	0.0002	ns	ns	0.005	ns	ns
deep vs shallow	0.005	0.01	0.01			
0.01g[d] vs 0.10g[d]	ns	0.05	ns			
0.50g[d] vs 0.10g[d]	0.02	ns	ns			
0.01g[d] vs 0.50g[d]	0.05	ns	ns			

plants.

The large 0.50g pellet had significantly lower uptake of added P after the first month of barley growth on both soil samples than the other granule size treatments (Table 4.15). The narrow distribution of MAP fertilizer in this treatment was probably responsible for the low uptake of added P. By the end of the second month the P uptake from the 0.50g granule size treatment was similar to treatments of other granule sizes. By the end of the third month the uptake of added P from the 0.50g granule size treatment was the same as the other granule size treatments for the Breton sample but was significantly higher than the other granule size treatments for the Paddockwood sample.

4.5.2. Discussion of the Effect of Granule Size of MAP Fertilizer on Phosphorus Uptake and Barley Growth

The similarity of the distribution between soil P fractions of different granule size treatments indicate the same reactions are occurring near the fertilizer pellet regardless of the size. One might expect, that with a larger surface area, more P of the smaller size treatment would become fixed. However, since the majority of added P remains in the plant available Resin-P form, no difference in crop P uptake is detected between granule size treatments.

P uptake by barley was generally unaffected by the granule size of MAP fertilizer. Differences that existed after the first month were gone after the second month in most cases. The lowering of the difference in uptake of added P from the soils shows the buffering effect the soil P cycle has. The solution form of MAP had significantly higher uptake of added P from the Breton sample after one month. This is probably the result of the greater initial P distribution resulting from solution application. The absence of any

significant increase after the second month probably results from the fact that in the other treatments, rooting located P sources and thus sufficient P was taken up.

4.5.3. Effects of Fertilizer Band Placement on P Uptake and Barley Growth

The P uptake of deep banded treatments on the Breton soil was also unaffected by MAP granule size (Table 4.12). The larger granule size treatment had lower uptake of added P after one and two months, for the same reasons as this granule size treatment had lower uptake in the shallow band treatments. The poor distribution of P lowers the probability of the plant roots from coming into contact with added P (Sander and Egball, 1988).

The deep banded MAP pellet treatments had significantly lower uptake of added P than the shallow banded treatments (Table 4.12). In addition to the low P uptake, barley yields were significantly lower (Table 4.13). Assuming that the distribution between soil P fractions in the soil near the deep banded pellets is similar to that near the of the shallow banded treatments, the only explanation for low P uptake and low yields must be the plant root not finding the P source soon enough. Roots definitely reach the P source, as evident in the P uptake values (Table 4.12), but clearly the plant is not able to absorb enough.

4.5.5. Effect of Organic Amendment on Uptake of P and Barley Growth

The uptake of added P from the treatments with organic amendments was significantly higher than without organic amendment in both Breton and Paddockwood samples. The peat amendment treatment also had significantly higher uptake of added P than the straw amendment. The higher uptake of added P from the treartments with organic amendments may be a result of lower contact between added P and the soil. The barley yields were not significantly greater despite the greater uptake of added P.

TABLE 4.13. Barley harvest weights of dry shoot material from Breton and Paddockwood soils for pellet size, pellet placement and organic amendment treatments.

Form of fertilizer	Harvest time periods (days)					
	BRETON			PADDOCKWOOD		
MAP[&]	30	60	90	30	60	90
	grams of shoot material/pot					
Control[s]	1.83	9.34	26.51	0.61	3.60	16.98
Solution P[#s]	2.54	10.48	30.16	1.73	9.41	25.16
0.01g[s]	2.50	11.13	29.94	1.55	8.98	24.78
0.10g[s]	2.51	11.83	29.25	1.56	9.00	24.90
0.50g[s]	2.51	11.03	30.86	1.35	8.91	24.39
Straw[s]	2.43	11.16	29.51	1.49	9.58	24.49
Peat[s]	2.34	10.98	29.52	1.83	9.63	25.87
0.01g[d]	1.08	9.20	25.83			
0.10g[d]	1.24	8.80	24.85			
0.50g[d]	1.05	7.20	25.20			

& Fertilizer MAP was added at a rate of 20 kg/ ha, and K2SO4 and NH4NO3 were added at rates of 20 and 50 kg/ha, respectively.
# Fertilizer was dissolved water and added as a band.
d Fertilizer was banded 10 cm below the seed row.
s Fertilizer was banded 2cm below and 2cm beside seed row.

Significance levels for various treatment contrasts from analysis of variance of barley harvest dry weights greenhouse experiment.

Orthogonal Contrasts	Harvest time periods (days)					
	BRETON			PADDOCKWOOD		
	30	60	90	30	60	90
cnt vs trmts	0.005	0.02	0.05	0.0001	0.0001	0.0001
soln vs granular	ns	ns	ns	ns	ns	ns
lo,hi vs mid	ns	ns	ns	ns	ns	ns
0.01g vs 0.50g	ns	ns	ns	ns	ns	ns
0.1g vs 0.1g + org	ns	ns	ns	ns	ns	ns
Peat vs Strw	ns	ns	ns	0.05	ns	ns
Nonorthogonal Contrasts						
0.01g[s] vs 0.10g[s]	ns	ns	ns	ns	ns	ns
0.50g[s] vs 0.10g[s]	ns	ns	ns	0.05	ns	ns
deep vs shallow	0.005	0.01	0.01			
0.01g[d] vs 0.10g[d]	0.01	ns	ns			
0.50g[d] vs 0.10g[u]	0.01	ns	ns			
0.01g[d] vs 0.50g[d]	ns	ns	ns			

4.5.6. Discussion of the Effect of Organic Amendments on Uptake of Phosphorus and Barley Growth

Putting the fertilizer pellet in a volume of peat/straw may have lowered the dissolution rate of the MAP granules. The organic material would have a lower matrix potential than the surrounding soil at field capacity causing water to move towards the organic volume. Therefore, the added P would only move out of the organic volume through diffusion against the current. This would lower the contact of added P with the soil and thus reduce the occurrence of reactions between soil and MAP fertilizer. Once a plant root finds the source of P there would be more P available thus allowing for higher P uptake.

There was no difference in barley yield despite the higher uptake of P from the treatments with peat amendment. Therefore, plants may save this excess P for grain fill.

5.0 Conclusion

Based on the results and observations of the studies of this thesis the following conclusions were drawn:

1) The reaction between soil and MAP fertilizer results in the release of cations into soil solution. The exchangeable cations are released from soil minerals through exchange with fertilizer ammonium. The low pH of soil solution containing MAP fertilizer initiates dissolution of soil clay minerals and of oxides and hydroxides. The dissolution of soil minerals may also release substantial amounts of ions into soil solution.

2) Added phosphate reacts with the ions that are released into soil solution. The reactions

of added phosphate with soil ions result in the production of P mineral precipitates. The calcium phosphate minerals Brushite, OCP and TCP form adjacent to soil minerals in voids near the application site of MAP fertilizer granules. Iron and manganese phosphate minerals precipitate on the surface of existing sesquioxidic nodules in the soil matrix.

3) Added P moves from readily available to less available soil P fractions with time after the addition of MAP fertilizer. However, near the application site of MAP fertilizer, the majority of P will remain in the Resin-P form even though the soil solution phosphate concentration decreases over this time period. The P that leaves the readily available form becomes adsorbed to inorganic and organic forms of iron, aluminium, and manganese; both components of the NaOH-P soil fraction. As the pH in soil solution increases from one hour to two months after the addition of MAP fertilizer, the solubility of calcium phosphate minerals decreases; therefore, forms of calcium phosphate mineral present as readily available P become less available forms associated with the HCl-P fraction.

4) The granule size of MAP fertilizer applied at a rate of 20 kg P ha^{-1} has a minimal effect on the efficiency of P uptake. The larger surface area and wider distribution of the smaller size (0.01g) fertilizer granules and of the solution forms of MAP fertilizer result in higher initial uptake of added P. Conversely the small surface area and poor distribution of the large (0.50g) fertilizer granule results in low initial uptake of added P. These effects only lasted for the first month because by the second month the P uptake was similar for all size treatments of MAP fertilizer granules.

5) Preventing contact of MAP fertilizer with soil minerals may increase the efficiency of P uptake. When granules of MAP fertilizer were encased in either straw or peat the efficiency of P uptake increased. The low density of the organic materials may prevent soil solution from readily moving into them. Therefore, water would move through the organic materials

slower and less often causing less MAP to dissolve thus lowering fertilizer contact with soil minerals.

6) The placement of bands of MAP fertilizer greatly affects the efficiency of P uptake by plants. Bands of MAP fertilizer within the vicinity of growing roots, 2 cm below and 2 cm beside the seed row, had a much higher effieiency of P uptake by plants than bands of MAP fertilizer placed 10 cm below the seed row. This effect lasted throughout the three months of barley growth.

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APPENDIX

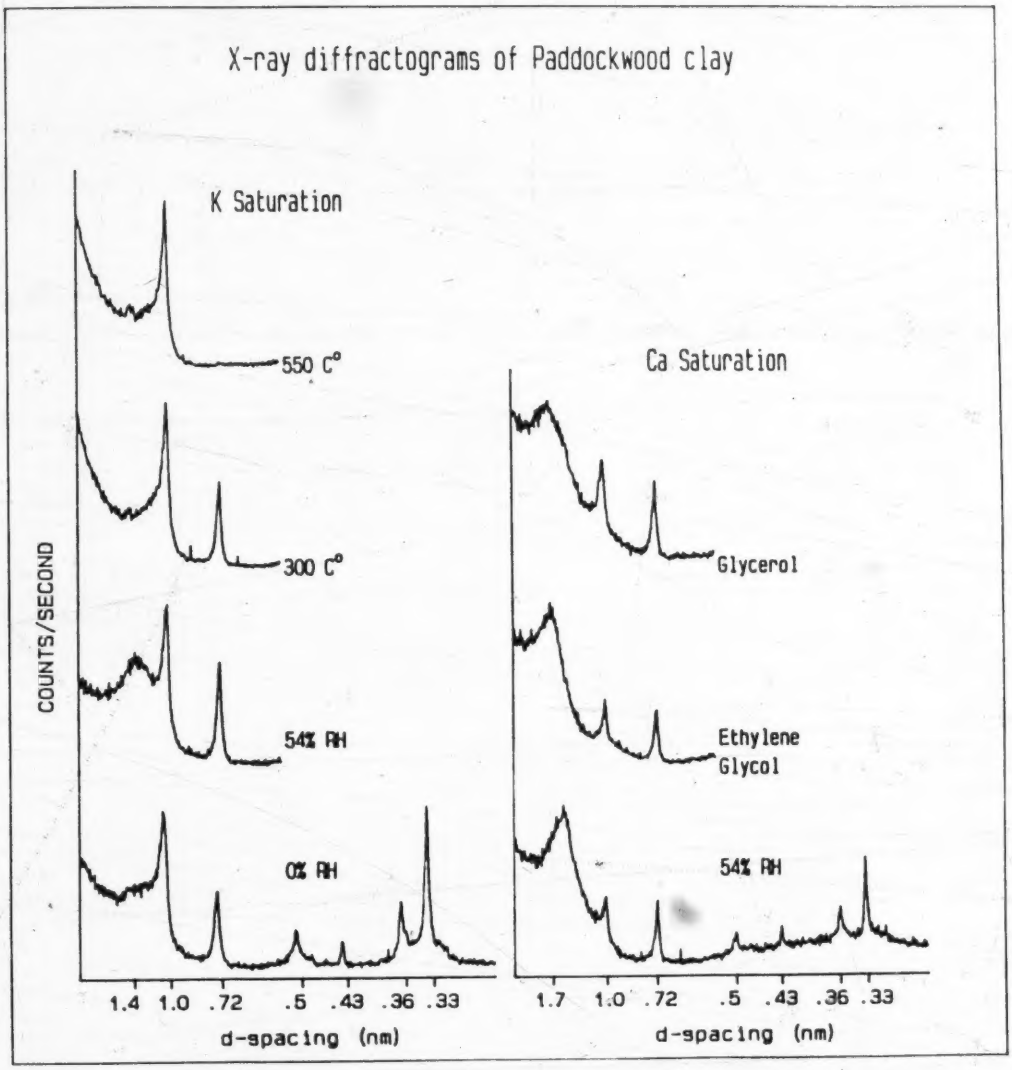

Figure A1. X-ray diffractograms of the clay separate from the Paddockwood sample.

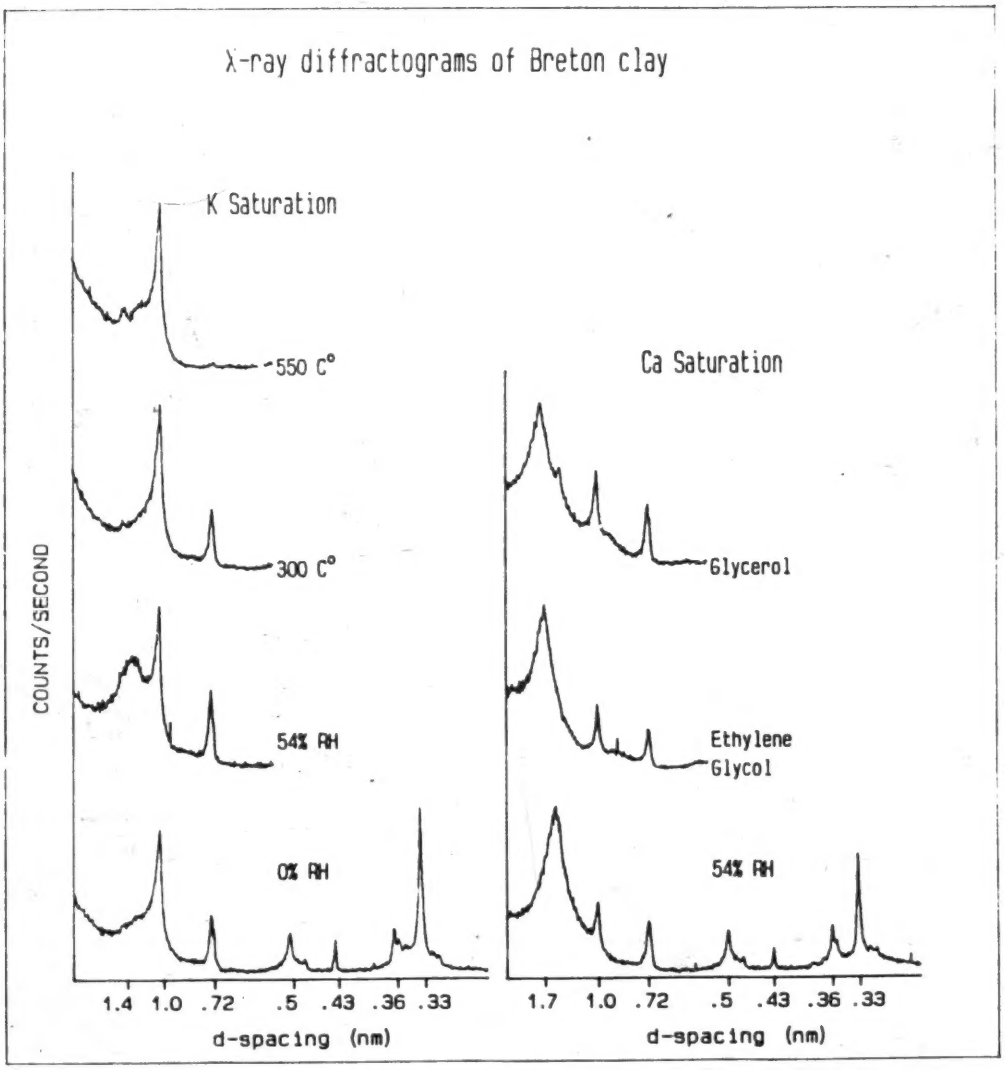

Figure A2. X-ray diffractograms of the clay separate from the Breton sample.